STUDIES IN CRYSTAL STRUCTURE

A THESIS

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PREFACE

The rather general title 'Studies in Crystal Structure' is given to this thesis because it embodies the results of investigations into two somewhat dissimila aspects of structure determination by x-ray crystallographic methods.

The introduction contains details of some less usual techniques which were used and also some comments on methods and theory.

The second part concerns investigations into the structure of the disordered crystals formed by tris-(methylsulphonyl) methane.

The elucidation of this structure was complicated by the disorder and necessitated the use of methods which would not ordinarily have been required had the structure been ordered.

The third part details the results of some preliminary investigations in sesquiterpenoid structure and the determination of the crystal structure of the alkaloid calycanthine. Although preliminary work on calycanthine utilised the technique of 'generalised projections,' the final elucidation of the structure resulted from the use of three-dimensional data and the 'heavy-atom method,' a technique which has become a standard method and which stems directly from Robertson and Woodward's work (1937, 1940) on the phthalocyanines.

PART I

INTRODUCTION

THE SUMMATION OF FOURIER SERIES IN TRIGONAL SPACE-GROUPS

In space groups possessing 3-fold and 6-fold axes the relationships among the indices of reflexions whose intensities are equal do not permit the ready derivation of formulae suitable for the calculation of Fourier series on digital computers. The Rollet Fourier program, which was used during the work to be described later, cannot calculate the coefficients and formulae necessary for the unique set of intensities in R3c.

Accordingly the reflexions were referred to a non-primitive cell of orthorhombic dimensions but monoclinic symmetry for which the Rollet program could be used. This cell has actually Cc symmetry with the $\underline{a}$ axis unique. This rather unusual choice was decided on in view of the fact that it is desirable to have the $\underline{a}$ axis as short as possible for efficiency in the Rollet program and also that it seemed appropriate to have sections perpendicular to the 3-fold axis and the Rollet program calculates sections perpendicular to the $\underline{c}$ axis.

The new cell is shown in Figure 1) and the equal intensities in Figure 2). It can be seen that the reciprocal axis a^*_2 is a 2-fold axis and has a mirror plane perpendicular to it, thus the Laue symmetry is effectively 2 / m.

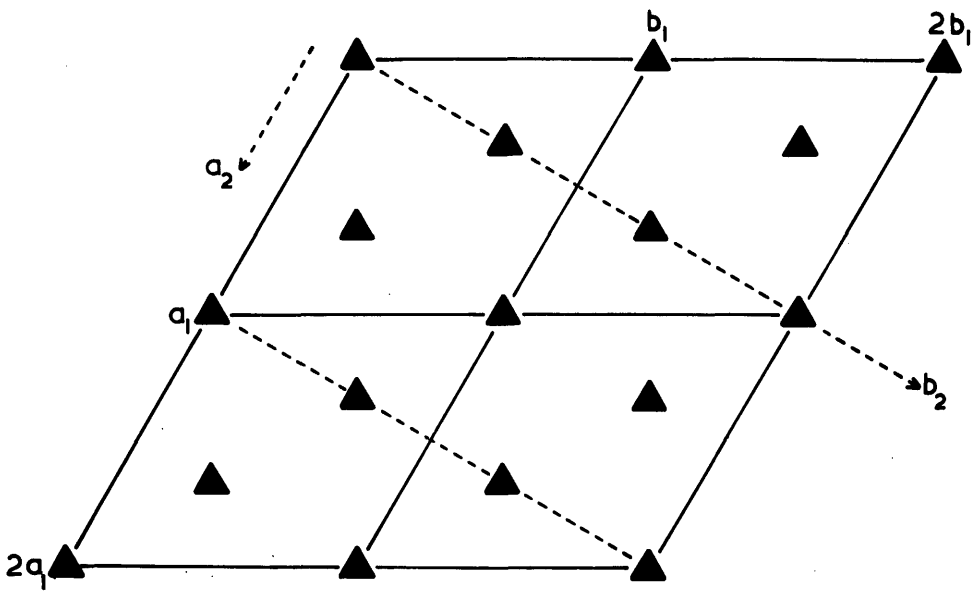


Figure 1.

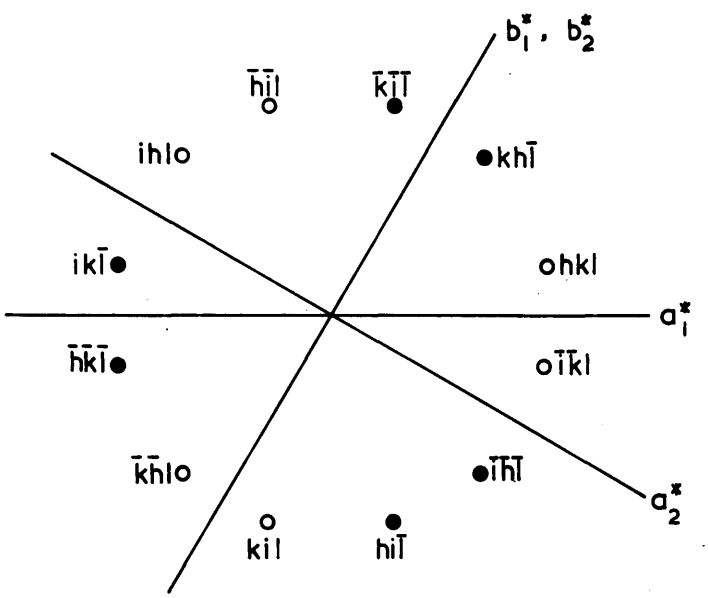


Figure 2.

The equations connecting the new axes with the old are:-

$$\vec{a}_2 = \vec{a}_1$$

$$\vec{b}_2 = \vec{a}_1 + 2\vec{b}_1$$

$$\vec{c}_2 = \vec{c}_1 \quad ;$$

and the old with the new:-

$$\vec{a}_1 = \vec{a}_2$$

$$\vec{b}_1 = -\tfrac{1}{2}\vec{a}_2 + \tfrac{1}{2}\vec{b}_2$$

$$\vec{c}_1 = \vec{c}_2$$

Thus the two transformation matrices, as in International Tables for X-ray Crystallography (1952) Volume I page 16, are.

$$\begin{matrix} 1 & 0 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad \begin{matrix} 1 & 0 & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{matrix}$$

The transformation for indices is the same as the transformation for axes.

The twelve equivalent reflexions for R3c, with the appropriate reciprocal axes are shown in Figure 2). The indices are as for R3c, where i is the conventional fourth index in hexagonal indexing; given by $i = -(h + k)$.

With the new cell we can state that

$$|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}| = |F_{h\bar{k}\bar{l}}|$$

reducing the twelve-fold set to three. Further reduction does not lead to simplification. The problem is then to generate with appropriate phase factors, the two extra reflexions necessary.

As there is no change of origin there are no changes in phase to be considered and the calculation of phases can be done with the original indices. Reference to the diagram indicates that reflexions $k_1 h_1 \bar{l}_1$ and $\bar{i}_1 \bar{k}_1 l_1$ should be generated from $h_1 k_1 l_1$ as it is desirable to have as few indices which vary in sign as possible. This choice ensures that h_2, k_2 are positive and l_2 can be positive or negative except that, when $k_1 > h$, k_2 will be negative for $\bar{i}_1 \bar{k}_1 l_1$ Hence in this case one should generate $\bar{i}_1 \bar{h}_1 \bar{l}_1$

Thus we have the table.

$k, \leqslant h,$		$k, > h,$
h k l	⟶ h, h + 2k, l	h k l
k h l	⟶ k, k + 2h, l	k h l
i k l	⟶ h + k, h − k, l	i h l ⟶ h + k, k − h, l.

The approach actually used was test $k, > h,$ and, if so, to generate k h $\bar{l}$ with appropriate A and B, replace h k l by this and carry out the rest of the transformations.

Reference to the structure factor expression shows the following relationships among A and B.

	l even		l odd	
	A	B	A	B
h k l	+	+	+	+
k h $\bar{l}$	+	−	−	+
$\bar{i}$ $\bar{k}$ l	+	+	−	−

A basic program was written for the computer 'Deuce' to carry out these operations when supplied with the results of a structure factor calculation in space-group R3c on the unique set of reflexions. The extra reflexions are generated and punched on to cards of the same format as the input data. The program also allows for the fact that the multiplicity of reflexions h00, h0l, 0kl, 00l, hh0, is less than twelve by omitting to calculate certain combinations where necessary. Although the program is only designed for

space-group R3c it could be modified readily for other trigonal space groups and, accordingly, is given in flow sheet form following this discussion.

The speed of the program is somewhat less than the punch-speed but of the order of one card a second output.

TRIGONAL GENERATOR FLOW SHEET. J.V. Silverton — ⑦

To generate the extra reflexions necessary to calculate a fourier summes in space gp R3c using Rollet's program.

I_{25} $I_{27}-13$ Link

2_{27} Read

$Q_{30}(I_{27}$ 27-15) } 27 gives PI = 1 if Laue1, PI in 17_2. otherwise PI = 0.

3_0 17_2-14

I_3 $25-19_3$ $[19_3$ = Le, Nz, Lo$]$ } Details from card read

4_6 17_3-10_8 (Δmc)

I_{11} 18_0-10_{20} (Δmc)

I_{23} $9_{25}-17_1$ (Δmc) Bring Q. inst

8_{28}(6PI) 17_1-O_5, 1

$Q_5(9_{25}$ 10 −14, 0, 0 (11) 4)

7_{11} (2PI) 17_2-O_{14}, 1

All data passed → 7_{12}

$Q_{26}(9_{26}$ 10− 15, 0, 3 (0), 8)

I_{24} $6_{27}-16$ $[6_{27}$ = 100:4BP$]$ Convert data to $X_1 X X X_2$ for punch-out program.

7_{29} $14-21_3$

7_1 $1-24$ ÷100

I_{26} $13-13$ [31,9]

I_5 9_7-16 $[9_7$ = 10,000:4BP$]$

7_8 21_2-14

I_{10} $15-21_3$

I_{13} $1-24$ ÷10,000

7_2 (2PI) 17_0-O_4, 1

$Q_4(9_{28}$ 14− 10, 0, 1 (0) 16)

I_{22} $13-13$ [24,24]

I_{16} $4-24$

I_{19} 21_2-15

7_5 (2PI) 17_3-O_7, 1

$Q_7(9_{27}$ 15 −10, 0, 10, (0) 19)

7_{22} $10_{20}-18_0$ (Δmc) ΔF, F, C, S → Data to DL 10 for punch out.

7_{23} 10_8-17_0 (Δmc) H, K, L, S^2

2_{11} 17_3-10_{19} S^2_3

8_{30} 18_0-10_4 (2mc) $\Delta F_1, F_1$

8_5 17_3-10_{11} S^2_2

8_{18} 18_0-10_{20} (2mc) $\Delta F_3, F_3$

8_{21} 17_3-10_3 S^2_1

8_3 18_0-10_{12} (2mc) $\Delta F_2, F_2$

8_{13} 17_0-13 Test K>H

8_{16} 17_1-26

7_{21} $13-27$

K<H → 8_{25} K>H → 8_{26}

Generate ortho-hex indices

8_{25}	$17_0 - 13$	
8_{29}	$13 - 10_0$	$H_1 = H$
8_0	$17_1 - 26$	
8_6	$13 - 10_{17}$	$K_3 = H - K$
8_{17}	$17_1 - 13$	
8_{22}	$13 - 10_8$	$H_2 = K$
8_8	$17_0 - 25$	
8_{12}	$13 - 10_{16}$	$H_3 = H + K$
7_{16}	$17_0 - 25$	
7_{20}	$13 - 10_9$	$K_2 = 2H + K$
7_9	$17_2 - 13$	
7_{14}	$13 - 10_{18}$	$L_3 = L$
7_{18}	$13 - 10_2$	$L_1 = L$
8_2	$30 - 13$	
8_4	$17_2 - 26$	
7_0	$13 - 10_{10}$	$L_2 = -L$
7_{10}	$17_0 - 13$	
7_{13}	$17_1 - 14$	
7_{17}	$24 - 25$	
7_{19}	$13 - 10_1$	$K_1 = 2K + H$
1_{21}	$18_2 - 10_6$	$C_1 = C$, $S_1 = S$

→ 7_1

Interchanges for K > H

8_{26}	$17_0 - 14$	
6_{29}	$17_1 - 15$	$K \rightleftarrows H$
8_1	$15 - 17_0$	
1_6	$30 - 13$	
1_8	$17_2 - 26$	
8_{10}	$13 - 17_2$	$L \to -L$
7_{15}	$14 - 17_1$	
1_{17}	$30 - 13$	
8_{19}	$19_3 - 28$	

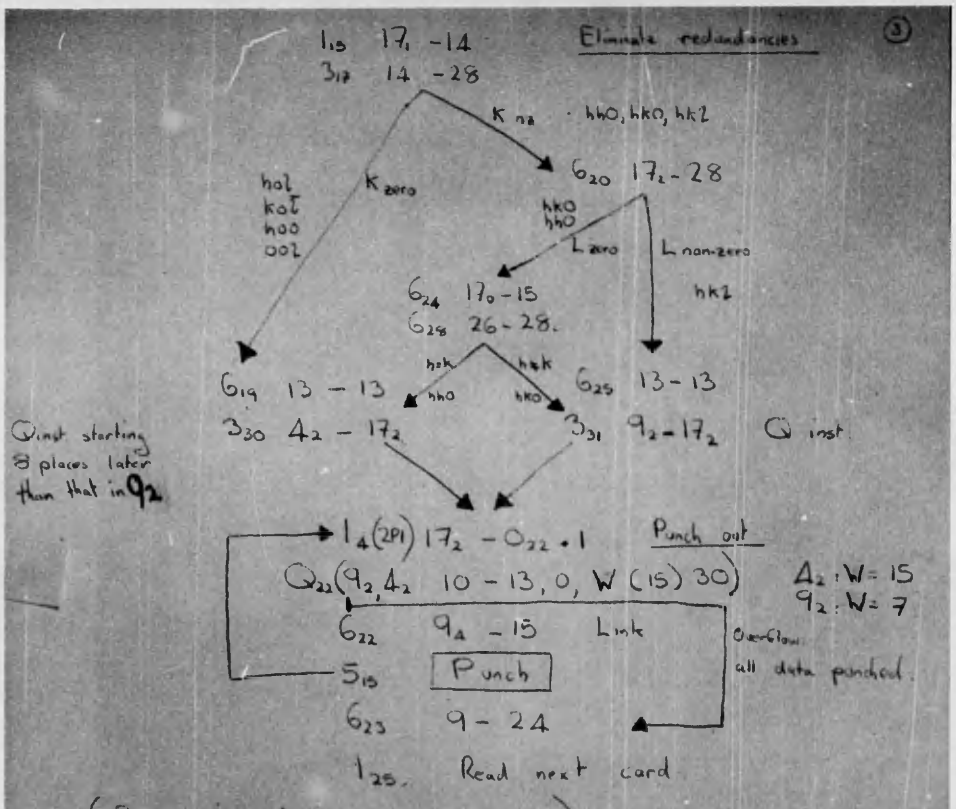
Leave 2 / Ladd n2

8_{23}	$18_3 - 26$	S to -S	8_{24}	$18_2 - 26$	C to -C
7_{27}	$13 - 18_3$		8_{31}	$13 - 18_2$	

8_{25} Return to normal program

7_7 $19_3 - 28$ — Ladd n2 / Leave 2

8_{14}	$18_2 - 13$		8_{15}	$30 - 13$	Change signs of C & S
1_{18}	$13 - 10_{22}$	$C_3 = C$	8_{20}	$18_2 - 26$	
4_9	$13 - 10_{14}$	$C_2 = C$	7_{25}	$13 - 18_2$	
7_{22}	$18_3 - 13$		7_{30}	$30 - 13$	
7_{28}	$13 - 10_{23}$	$S_3 = S$	7_0	$18_3 - 26$	
7_{24}	$30 - 13$		7_3	$13 - 18_3$	
7_{26}	$18_3 - 26$				
7_{31}	$13 - 10_{15}$	$S_2 = -S$			
1_{16}					



(9_4 is 1, 13-13, 0, 0, 4)

1. Output uses sub-routine P1A, # 130, in DL. 5.6

a) First digit to be punched in col 17, P1 in 5_{18}, 6_{18}

Layout of card. 6_{1A} 17 x 19 xx 22 xx 25 xx 28 xxxx 33 xxxx 38 xxxx 43 xxxx

27 BP in data 5_1. W = 54-31 = 23

Maximum error is 3 in last places . . round off is P6, P7 in 5_6

Process takes longer than punch routine allows; clear instruction 1_{20} is inserted between 5_{11} and 1_{30} (1 9-24, 0, 8)

Multiplicity will be correct if only independent reflexions included. [hk0 or kh0, but not both; h00 or 0k0, but not both]

Certain redundant reflexions, generated in special cases, are removed by the sequence starting in 1_{15}. The principle is that only $H_2 K_2 L_2$ . . . . and $H_3 K_3 L_3$ . . . . are punched for h0l, 0kl, h00, 00l, hh0.

ELECTRON DENSITY EXPRESSION FOR ORTHOHEXAGONAL MONOCLINIC SPACE GROUP

Referred to the indices of the orthohexagonal space group, the reflexions we wish to consider are $h_2\, k_2\, l_2$, $\bar{h}_2\, \bar{k}_2\, \bar{l}_2$, $h_2\, \bar{k}_2\, \bar{l}_2$.

The R3c reflexion corresponding to $h_2\, \bar{k}_2\, \bar{l}_2$ is $h, i, \bar{l}$, and reference to the structure factor expression shows that

$A_{hi\bar{l}} = A_{hkl}$ for l even $\quad B_{hi\bar{l}} = -B_{hkl}$ for l even

$= -A_{hkl}$ for l odd $\quad = B_{hkl}$ for l odd.

and, of course, as always

$$A_{\bar{h}\bar{k}\bar{l}} = A_{hkl} \qquad B_{\bar{h}\bar{k}\bar{l}} = -B_{hkl}$$

Starting with the usual electron density expression and dropping subscripts on indices,

$$\rho(xyz) = \frac{1}{V_c} \sum_h \sum_{-\infty}^{\infty}{}_k \sum_l F_{hkl} \exp -2\pi i (hx + ky + lz)$$

Using the trigonometric form of an exponential and eliminating $\bar{h}\ \bar{k}\ \bar{l}$ and therefore $h < 0$ we have

$$\rho(xyz) = \frac{2}{V_c} \sum_0^{\infty} h \sum_{-\infty}^{\infty} k \sum_l A_{hkl} \cos 2\pi(hx+ky+lz) + B_{hkl} \sin 2\pi(hx+ky+lz)$$

$$= \frac{2}{V_c} \sum_0^{\infty} h \sum_0^{\infty} k \sum_{-\infty}^{\infty} l \Bigg\{ \overset{\text{even}}{\downarrow} A_{hkl}\left[\cos 2\pi(hx+ky+lz) + \cos 2\pi(hx-ky-lz)\right]$$

$$+ B_{hkl}\left[\sin 2\pi(hx+ky+lz) - \sin 2\pi(hx-ky-lz)\right] \Bigg\}$$

$$+ \Bigg\{ \overset{l \text{ odd}}{A_{hkl}}\left[\cos 2\pi(hx+ky+lz) - \cos 2\pi(hx-ky-lz)\right]$$

$$+ B_{hkl}\left[\sin 2\pi(hx+ky+lz) + \sin 2\pi(hx-ky-lz)\right] \Bigg\}.$$

$$\therefore \rho(xyz) = \frac{4}{V_c} \sum_{0}^{\infty}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} \left\{ \begin{matrix} l \text{ even} \\ A_{hkl}[\cos 2\pi hx \cos 2\pi(ky+lz)] \\ + B_{hkl}[\cos 2\pi hx \sin 2\pi(ky+lz)] \end{matrix} \right\}$$

$$+ \left\{ \begin{matrix} l \text{ odd} \\ -A_{hkl}[\sin 2\pi hx \sin 2\pi(ky+lz)] \\ + B_{hkl}[\sin 2\pi hx \cos 2\pi(ky+lz)] \end{matrix} \right\}.$$

$$= \frac{4}{V_c} \sum_{0}^{\infty}\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} \left\{ \begin{matrix} l \text{ even} \\ A_{hkl} \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz \\ - A_{hkl} \cos 2\pi hx \sin 2\pi ky \sin 2\pi lz \\ + B_{hkl} \cos 2\pi hx \sin 2\pi ky \cos 2\pi lz \\ + B_{hkl} \cos 2\pi hx \cos 2\pi ky \sin 2\pi lz \end{matrix} \right\}$$

$$+ \left\{ \begin{matrix} l \text{ odd} \\ - A_{hkl} \sin 2\pi hx \sin 2\pi ky \cos 2\pi lz \\ - A_{hkl} \sin 2\pi hx \cos 2\pi ky \sin 2\pi lz \\ + B_{hkl} \sin 2\pi hx \cos 2\pi ky \cos 2\pi lz \\ - B_{hkl} \sin 2\pi hx \sin 2\pi ky \sin 2\pi lz \end{matrix} \right\}.$$

GENERALIZED PROJECTIONS

The method of generalized projections has been found useful for the derivation of the third coordinate in structures where only one good projection is available and also for the resolution of overlapped projections where the overlapping molecules are separated by a rational distance. Dyer (1951) and Cochran & Dyer (1952)).

It was also applied by Fridrichsons & Mathieson (1955) in a very elegant determination of the structure of a complex organic molecule without the use of full three-dimensional data.

The principles of the method are detailed by Lipson & Cochran (1953).

In the general case we have,

$$\rho(xyz) = \frac{1}{V}\sum_{-\infty}^{\infty}\sum\sum F_{hkl} \exp -2\pi i(hx+ky+lz) \quad \text{——1}$$

The generalized projection of this distribution on a plane perpendicular to the g axis is defined as

$$\rho_L(xy) = c\int_0^1 \rho(xyz) \exp[2\pi i Lz]\,dz \quad \text{——2}$$

where one wishes to use the hk L data.

Substituting for $\rho(xyz)$ from 1 and using the fact that

$$\int_0^1 \exp[2\pi i(L-l)dz = 1 \quad \text{when } l = L$$
$$= 0 \quad \text{when } l \neq L$$

we have,

$$\rho_L(xy) = \frac{1}{A}\Sigma\Sigma F(hkl)\exp[-2\pi i(hx+ky)] \qquad 3$$

Now, $F_{hkl} = A_{hkl} + i\,B_{hkl}$ and making a corresponding definition for $\rho_L(xy)$ we have,

$$\rho_L(xy) = C_L(xy) + i\,S_L(xy) \qquad 3a$$

Thus we obtain from 3,

$$C_L(xy) = \frac{1}{A}\Sigma\Sigma A_{hkL}\cos 2\pi(hx+ky) + B_{hkL}\sin 2\pi(hx+ky) \qquad 4$$

$$S_L(xy) = \frac{1}{A}\Sigma\Sigma B_{hkL}\cos 2\pi(hx+ky) - A_{hkL}\sin 2\pi(hx+ky) \qquad 5$$

A 'modulus projection' (after Fridrichsons & Mathieson) may be evaluated which is equivalent to the normal electron density projection and this can be compared with the normal projection with a view to finding areas of density which are common to both. The rationale here is that errors in the two projections are unlikely to be the same and common areas of density are less likely to be spurious.

The modulus projection may be defined as

$$\rho_{mod} = |(C_L^2 + S_L^2)^{\frac{1}{2}}|$$

The comparison with the usual projection can be done by the Buerger 'minimum function' or similar functions.

A very useful property of the generalized projection, as mentioned earlier, is the determination of the third coordinate of atoms in a projection.

This follows from the fact that the height of a peak in C_L and S_L is proportional to $\cos 2\pi Lz$ and $\sin 2\pi Lz$ respectively. It follows from this that peaks can be positive or negative and thus a decision can sometimes be made as to which atoms belong to each of two overlapping molecules at different heights. In Cochran & Dyer's (1952) work, there were two molecules of diglycyl glycine ethyl ester hydrobromide at relative heights of 0 and $\frac{1}{2}$, and, in the C_1 (yz) projection, the atoms of one molecule gave positive peaks and the other negative ones.

If one makes use of the fact that, with spherically symmetric atoms,

$$F_{hkL} = \sum_{j=1}^{N} f_j(hkL) \exp -2\pi i(hx+ky).$$

Substituting in 3 and using 3a we have

$$C_L(xy) = \sum_{j=1}^{N} \sigma_{jL}(x-x_j, y-y_j) \cos 2\pi Lz$$

$$S_L(xy) = \sum_{j=1}^{N} \sigma_{jL}(x-x_j, y-y_j) \sin 2\pi Lz$$

where $\sigma_{jL}(xy) = \frac{1}{A} \sum_{hk} f_j(hkl) \exp[-2\pi i(hx+ky)]$

Thus from the ratio $\frac{C_L}{S_L}$ we can determine $\cot 2\pi Lz_j$ and hence z_j.

APPLICATION OF GENERALISED PROJECTIONS IN $P2_12_12_1$.

The C_H and S_H functions can be derived as follows. It might be as well to show that $\int_0^1 \exp -2\pi i(h-H)x\,dx$ is 0 or 1 depending on whether $h \neq H$ or $h = H$ respectively.

$$\int_0^1 \exp -2\pi i(h-H)x\,dx = \int_0^1 \exp -2\pi i(0)x\,dx = 1, \text{ if } h = H$$

$$= \int_0^1 (\cos 2\pi(h-H)x - i\sin 2\pi(h-H)x)dx, \text{ if } h \neq H$$

$$= \frac{1}{2\pi(h-H)}\left[\sin 2\pi(h-H)x + i\cos 2\pi(h-H)x\right]_0^1$$

$$= \frac{1}{2\pi(h-H)}\left[\sin 2\pi(h-H) + i\cos 2\pi(h-H) - i\right]$$

$$= 0, \text{ as } (h-H) \text{ is an integer.}$$

We may write $\rho_H(yz) = \frac{1}{A_{bc}} \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} \exp -2\pi i(ky + lz)$.

Then $C_H = \frac{1}{A} \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} \left[A_{Hkl}\cos 2\pi(ky + lz) + B_{Hkl}\sin 2\pi(ky + lz)\right]$.

$S_H = \frac{1}{A} \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} \left[B_{Hkl}\cos 2\pi(ky + lz) - A_{Hkl}\sin 2\pi(ky + lz)\right]$.

For $P2_12_12_1$ the necessary relationships among the phase angles for reflexions possessing the same intensity are as follow on the next page.

	h k l	h $\bar{k}$ l	h k $\bar{l}$	h $\bar{k}$ $\bar{l}$
h + k (even, k + l (even	+ α	− α	− α	+ α
(even, (odd	+ α	π − α	π − α	+ α
(odd, (even	+ α	− α	π − α	π + α
(odd, (odd	+ α	π − α	− α	π + α

And thus the corresponding signs to be attached to A & B are

	h k l		h k l		h k l		h k l	
h + k (even, k + l (even	A	B	A	B	A	B	A	B
	+	+	+	−	+	−	+	+
(even, (odd	+	+	−	+	−	+	+	+
(odd, (even	+	+	+	−	−	+	−	−
(odd, (odd	+	+	−	+	+	−	−	−

Then for h + k even k + l even

$$C_H = \frac{1}{A}\sum_0^\infty{}_k\sum_0^\infty{}_l \Big\{ A_{hkl}\big[\cos 2\pi(ky+lz)+\cos 2\pi(-ky+lz)+\cos 2\pi(ky-lz)+\cos 2\pi(-ky-lz)$$
$$+B_{hkl}\big[\sin 2\pi(ky+lz)-\sin 2\pi(-ky+lz)-\sin 2\pi(ky-lz)+\sin 2\pi(-ky-lz)\big]\Big\}.$$

$$= \frac{2}{A}\sum_0^\infty{}_k\sum_0^\infty{}_l\, A_{hkl}\big[\cos 2\pi(ky+lz)+\cos 2\pi(ky-lz)\big]$$

$$= \frac{4}{A}\sum_0^\infty{}_k\sum_0^\infty{}_l\, A_{hkl}\cos 2\pi ky \cos 2\pi lz.$$

$$S_H = \frac{1}{A}\sum_0^\infty{}_k \sum_0^\infty{}_l \Big\{ B_{Hkl}\big[\cos 2\pi(ky+lz) - \cos 2\pi(-ky+lz) - \cos 2\pi(ky-lz) + \cos 2\pi(-ky-lz)\big] - A_{Hkl}\big[\sin 2\pi(ky+lz) + \sin 2\pi(-ky+lz) + \sin 2\pi(ky-lz) + \sin 2\pi(-ky-lz)\big]\Big\}$$

$$= \frac{2}{A}\sum_0^\infty{}_k \sum_0^\infty{}_l B_{Hkl}\big[\cos 2\pi(ky+lz) - \cos 2\pi(ky-lz)\big]$$

$$= -\frac{4}{A}\sum_k \sum_l B_{Hkl} \sin 2\pi ky \sin 2\pi lz .$$

Similarly for h + k even , k + l odd ,

$$C_H = -4A \sin 2\pi ky \sin 2\pi lz \; ; \; S_H = 4B \cos 2\pi ky \cos 2\pi lz .$$

For h + k odd, k + l even ,

$$C_H = 4B \sin 2\pi ky \cos 2\pi lz ; \; S_H = -4A \cos 2\pi ky \sin 2\pi lz .$$

For h + k odd, k + l odd ,

$$C_H = 4B \cos 2\pi ky \sin 2\pi lz ; \; S_H = -4A \sin 2\pi ky \cos 2\pi lz .$$

Combining these, using the symbols o and e for odd and even we have:-

$$C_H = \frac{4}{A}\sum_0^\infty{}_k \sum_0^\infty{}_l \big[\cos 2\pi ky \,(A^{ee}_{Hkl} \cos 2\pi lz + B^{oo}_{Hkl} \sin 2\pi lz) + \sin 2\pi ky \,(B^{oe}_{Hkl} \cos 2\pi lz - A^{eo}_{Hkl} \sin 2\pi lz)\big].$$

$$S_H = \frac{4}{A}\sum_0^\infty{}_k \sum_0^\infty{}_l \big[\cos 2\pi ky \,(B^{eo}_{Hkl} \cos 2\pi lz - A^{ee}_{Hkl} \sin 2\pi lz) - \sin 2\pi ky \,(B^{oe}_{Hkl} \sin 2\pi lz + A^{oo}_{Hkl} \cos 2\pi lz)\big].$$

This is a suitable form for calculation with Beevers-Lipson strips.

THE OPTICAL DIFFRACTOMETER

This device which has proved very useful in investigating the disorder in tris (methylsulphonyl) methane originally was used by Bragg as what he referred to as an "X-ray microscope."

In this case the optical transform of a weighted reciprocal lattice, when all phases could be assumed to be the same (a heavy atom at the origin) was used to produce directly a picture of several unit cells.

Later developments were due to Lipson & Taylor mainly.

The apparatus is shown in Figure 3).

Light from the high pressure mercury lamp A is focussed via lens and prism on to pinhole B. The light is filtered to produce nearly monochromatic light (yellow; $\lambda \simeq 5790$Å.) The pinhole B then acts as a nearly monochromatic small source (radius variable; usually 25 μ - but 12½ and 6 μ available). B is at the focus of lens L_1 which thus produces parallel light. The Fraunhofer diffraction pattern of an object placed at O is thus produced. This is brought to a focus by lens L_2, via a surface silvered mirror E, in the focal plane F, of microscope G. A 16 mm. camera may replace the microscope.

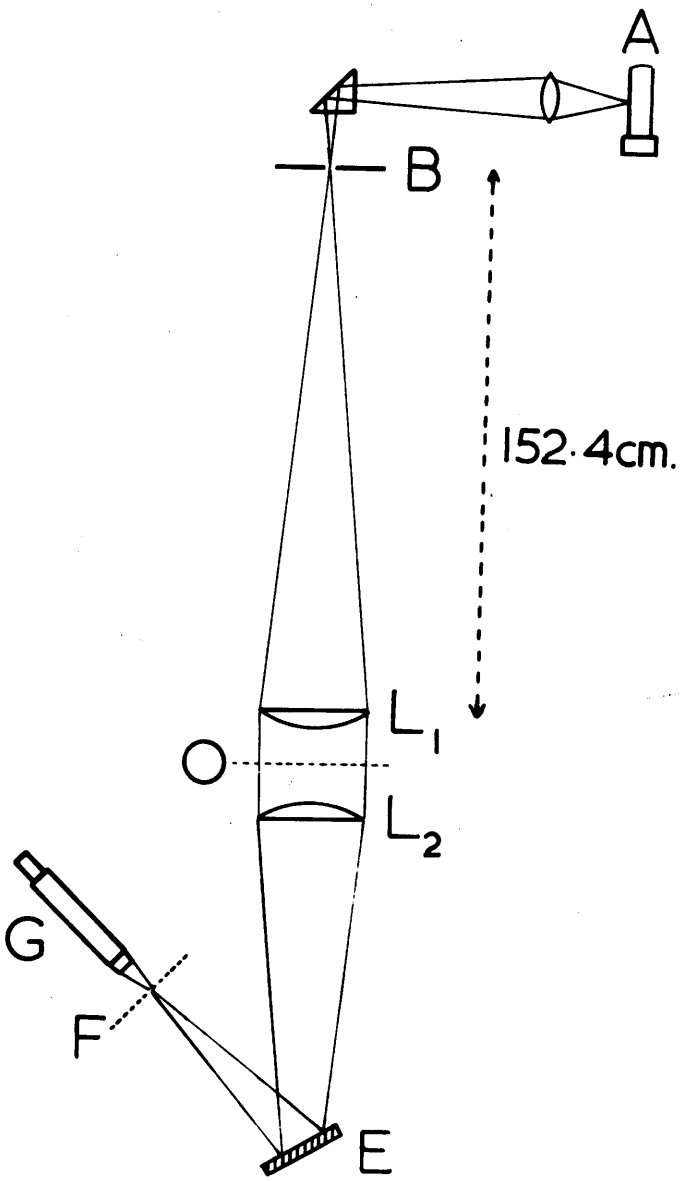


Figure 3.

NOTE. "Fraunhofer diffraction" corresponds to a light source at a great distance or else to diffraction by a source whose light has been made parallel by a lens system. Diffraction by closer sources is "Fresnel diffraction."

The Fraunhofer diffraction pattern is essentially a Fourier transform of the object placed at O. Thus optically, transforms of molecules represented by holes in opaque masks may be obtained readily and such transforms can be compared with the reciprocal structure of a crystal in order to determine molecular orientation. It should be pointed out that, if the structure does not possess a centre of symmetry, the transform is complex and the optical pattern is the modulus of the transform. If a number of molecules are arranged on a lattice, the transform corresponds to the reciprocal structure and can be compared with, for example, a precession photograph.

Another way of regarding the diffractometer is from the sphere of reflexion stand-point; vide Lipson & Taylor (1958). The units in a reciprocal structure can be assigned a volume; as opposed to the reciprocal lattice which is, of course, composed of points.

The Ewald construction for X-ray diffraction shows that only those units of the reciprocal structure which lie on the surface of the reciprocal sphere, radius $1/\lambda$, are observable. However if λ is small enough compared with the object, the reciprocal of the object can be totally within the sphere. The intersection of the reciprocal structure and the sphere is then equivalent to a plane through the origin of the reciprocal structure and thus any one setting allows exploration of a plane section of the reciprocal structure. This happens, for example, in electron diffraction where any one setting will give a single crystal diffraction pattern ($\lambda \simeq 0.05\text{Å}$) and is also equivalent to the situation in the optical diffractometer (radius of reciprocal sphere is ca. $\frac{1}{6000\text{Å}}$ i.e. $1.6 \times 10^{4}\text{cm.}^{-1}$ and the reciprocal of a typical diffracting unit is ca. 1 cm.^{-1}).

THE PEPINSKY X-RAY ANALOGUE COMPUTER - X-RAC.

This computer is designed to perform two-dimensional fourier summations by means of the addition of suitably generated electrical potentials. The amplitudes of the terms for a fourier summation can be set by means of rheostats and, once the coefficients are set, the summation is practically instantaneous; the results being displayed on a television screen in the form of a contour map with a superimposed grid.

The machine was described by Pepinsky (1950) in the report of the first conference on X-ray computing methods and the phase Problem and has been operating since 1948.

The machine can also be used to produce sections of a three-dimensional fourier summation by performing an initial one-dimensional summation, for each section, on a digital computer, and then using the results of this for input to X-RAC.

THE ROBERTSON DIGITAL MECHANICAL COMPUTER FOR FOURIER SYNTHESIS - RUFUS

This device was used fairly extensively in the two-dimensional work to be described in the thesis. It was originally described by Robertson in 1954 and the machine, as built, embodies simplifications outlined by Robertson in 1955.

Descriptions of the machine are given by Robertson (1960) in a paper delivered at the Conference on 'Computing Methods and the Phase Problem in X-ray Crystal Analysis,' Glasgow, 1960.

The basic idea is that the appropriate sine and cosine functions are generated by means of suitable gear ratios, the amplitudes are generated by integral revolutions of driving shafts and the resulting digital summation performed by differential gears. The output is by means of revolution counters.

NOTE ON PRODUCTION OF OPTICAL INTERFERENCE BY INCOHERENT SOURCES.

ref. Born & Wolf (1959) Principles of Optics. Pergamon.

In general the variation in intensity in a single beam of light may be described in terms of changes in the cross sectional area of a tube of rays. When two or more light beams are superposed, the distribution of intensity can no longer be described in such a simple manner. The intensity may vary from point to point such that we may have maxima which exceed the sum of the intensities in the beams and minima which may be zero.

In a strictly monochromatic beam from a single source the fluctuations of amplitude and phase are strictly correlated i.e. the light is coherent. However light produced from a real physical source is never strictly monochromatic and it can be seen from atomistic theory that the amplitude and phase undergo irregular fluctuations much too rapid for the eye or an ordinary physical detector to follow. The fluctuations from various parts of a finite source may be correlated partially, the correlation depending on distance apart of the elementary radiators i.e. the atoms in the source. Such light is thus partially coherent. The radiation from two separate sources is completely uncorrelated and the light is thus incoherent.

Elementary interference theory using perfectly monochromatic, coherent light shows that the interference pattern depends on phase differences between beams. Thus, if the relative phases of two beams change, the positions of the maxima in the interference function will shift and this implies that, with incoherent radiation, although in a very small instant of time there may be interference, the interference pattern will effectively be smeared out.

The facts that two separate light sources do not give interference and that light from a single small source, e.g. a pinhole, when divided into two or more beams does, were of course noticed early on. The production of interference was one of the arguments for the wave-nature of light. It is however only recently that a rigorous theory of optical interference by partially coherent light has been worked out.

Most text-books when discussing interference use the concept of coherent light and it seems profitable to discuss the question of real sources further as the fact that real light sources are incoherent radiators seems generally to be avoided.

For a real source the important point is that light from such a source is partially coherent and the degree of coherence may be correlated with the breadth of a spectral

line. The analysis is due mainly to E. Wolf (1955, 1958).

The most important conclusion is that where suitable definitions of time averages are taken the following equation applies

$$\Delta\tau\Delta\upsilon \sim \frac{1}{4\pi} \quad \text{where} \quad \begin{array}{l} \Delta\tau \text{ is the coherence time} \\ \Delta\upsilon \text{ is frequency spread} \\ \text{in a spectral line.} \end{array}$$

The arguments for this deduction are similar to those used in the derivation of the Heissenberg uncertainty principle. The important concept here is $\Delta\tau$ which may be regarded as a short time interval in which the light from a real source can be regarded as coherent. The equation thus correlates this time with the observable frequency spread of a spectral line. It follows that, in an interference experiment, if the path differences between interfering beams are such that they are much less than the coherence length ($= C\,\Delta\tau$) optical interference will be shown. Providing that this condition holds (which is true for most interference experiments with the interference taking place at a large distance from the light source) all that must be considered is the degree of coherence available with a given finite source under the experimental

conditions.

An interesting development in recent years has been the laser producing a beam of almost completely monchromatic light which it follows must be almost completely coherent, so that we do now have natural sources of coherent light and in fact optical interference from separate sources has recently been demonstrated.

The first investigations in the theory of partially coherent light are probably those of Verdet (1865).

Through the years the names of Michelson, von Laue and Berek have been associated with work on this topic.

A new stage in development came in 1934 when van Cittert determined the joint probability distribution for the light disturbances at two points on a screen illuminated by an extended primary source. In a later paper he determined the probability distribution for light disturbances at any one point at two different instants of time.

Zernike in 1938 used a different approach and determined a "degree of coherence" in a manner related to experiment. The approach, although simpler is for most purposes equivalent to van Cittert's.

The theory was simplified further by Hopkins (1951) and applied to the study of image formation and resolving power.

Further and much more rigorous development is detailed in Wolf's paper of 1955 and independently by Blanc-Lepierre & Dumontet (1955).

An important consequence of what may be called the van Cittert-Zernike theorem is the determination of the diameter of the circular area that is illuminated almost coherently by a quasi-monochromatic uniform source of angular radius α which is $0.16\,\bar{\lambda}/\alpha$. This theorem assumes that the path differences are less than the coherence length. A departure of 12% for coherence is taken as the minimum acceptable value.

Wolf and Born consider the optical diffractometer on a basis of this theorem for two pinholes in the mask. The van Cittert-Zenike theorem shows that the degree of coherence

$$\mu_{12} = \left(\frac{2\,J_1(v)}{v}\right) e^{i\psi}$$

where $v = \frac{2\pi\rho}{\bar{\lambda} R}\sqrt{(X_1 - X_2)^2 + (Y_1 - Y_2)^2}$

and $\psi = \frac{2\pi}{\bar{\lambda}}\left[\frac{(X_1^2 + Y_1^2)^2 - (X_2^2 + Y_2^2)^2}{2R}\right]$

and ρ is the source radius, R the source distance, and X, Y the coordinates of the pinholes. J_1 is the Bessel function of the first kind and first order.

One implication of this is that the degree of coherence will fall to zero with increasing distance apart of the pinholes and then rise again to a small value. This is a consequence of the shape of the Bessel function. The effects are brought out well in a paper of Thompson & Wolf (1957) where photographs of the appropriate pinhole tranforms are shown.

One further comment is that it is interesting to the author, that, although optical interference by natural light sources has been demonstrated over a period of centuries, it is only very recently that the subject has been treated rigorously.

APPLICATION OF PARTIAL COHERENCE THEORY TO X-RAY DIFFRACTION

a) $$\Delta\tau\,\Delta\upsilon \sim \frac{1}{4\pi}$$

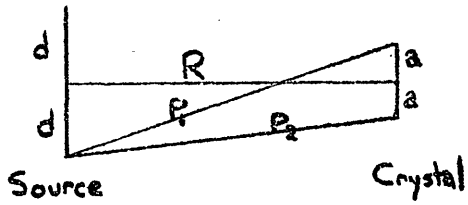
for Cu $K\alpha$; $\bar{\lambda} = 1.542$, $\Delta\lambda = 0.00060$ Å

$$c\,\Delta\tau\,\frac{\Delta\upsilon}{c} = \Delta L\,\frac{\Delta\lambda}{\lambda^2} \sim \frac{1}{4\pi} \qquad \text{since } \frac{c}{\Delta\upsilon} = \frac{\bar{\lambda}^2}{\Delta\lambda}$$

$$\Delta L \sim \frac{\lambda^2}{4\pi\Delta\lambda} = \frac{1.542^2}{4\pi \times 0.00060} = 312\,\text{Å}$$

Thus path differences in an interference experiment with Cu K_α radiation should be much less than 300Å for true interference.

b) Consideration of source size and path difference.



d = source radius

a = half distance between pinholes in optical experiment

R = source to object distance

Assuming that we only consider the strong and essentially parallel beam produced by a collimator, we can consider the source as the same size as the pinholes in a collimator.

Path difference to two extremes of diffracting object

$$= P_1 - P_2 = \left[R^2+(d+a)^2\right]^{\frac{1}{2}} - \left[R^2+(d-a)^2\right]^{\frac{1}{2}}$$

$$= \left[R^2+d^2+a^2+2ad\right]^{\frac{1}{2}} - \left[R^2+d^2+a^2-2ad\right]^{\frac{1}{2}}$$

$$= R\left[\left(1+\frac{d^2+a^2+2ad}{R^2}\right)^{\frac{1}{2}} - \left(1+\frac{d^2+a^2+2ad}{R^2}\right)^{\frac{1}{2}}\right]$$

$$\doteq R\left[1+\frac{d^2+a^2+2ad}{2R^2} - 1 - \frac{d^2+a^2-2ad}{2R^2}\right]$$

$$= \frac{R.4ad}{2R^2} = \frac{2ad}{R}$$

Taking an average size for a crystal mosaic unit of 3×10^3 Å

Source radius 0.2 mm : $\Delta P = \frac{2 \times 0.2 \times 10^7 \times 3 \times 10^3}{10^9} = 12$ Å

$R \sim 10$ cm.

Source radius 0.5 mm: $\Delta P = 30$ Å

These obey the condition that path differences should be much less than the coherence length.

c) Diameter of circle of coherence for X-rays.

Using the formula $\frac{0.16\bar{\lambda}}{\alpha}$

we have for a source radius 0.2 mm and at distance 10 cm;

diameter of circle of coherence = $\frac{0.16 \times 1.542 \times 10^{9}}{2 \times 10^{6}}$

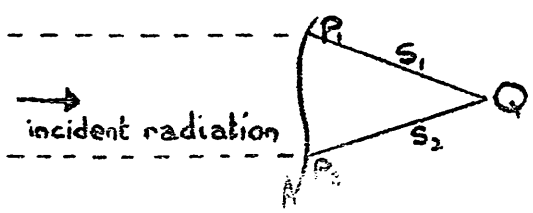
$= 123 \text{Å}$, for Cu $K\alpha$ X-radiation.

Another consequence of the van Cittert - Zernike theorem is that mutual coherence falls to zero at $\frac{0.61\bar{\lambda}}{\alpha}$ and therefore two scattering points 468 Å apart will have zero coherence.

This is considerably less than the usual estimate for mosaic block size viz. 3×10^{3} Å. The usual calculation for this size assumes coherence ratios of 1 and it could be enlightening to evaluate the integral expressing propagation of coherence with the true coherence ratios. The integral expressing intensity at a point Q from diffraction by a series of points (due to Zernike) is as follows

$$I(Q) = \iint_{A\,A} \sqrt{I(P_1)}\sqrt{I(P_2)}\,\mu(P_1P_2)\,\frac{e^{i\bar{k}(s_1-s_2)}}{s_1 s_2}\,\Lambda_1\Lambda_2^{*}\,dP_1\,dP_2$$

for the conditions as in the diagram



A is the arbitrary surface on which P_1, P_2 lie.

Λ is an inclination factor.

In effect the intensity is considered as a summation over all pairs of points P_1P_2 allowing for the coherence factor

As an experiment a linear set of diffracting objects 10 Å apart was considered on a basis of the above equation.

For a line 400 Å long and Cu K_α radiation, Q being ca. 5 cm. away.

$$\frac{\text{Intensity at Q}}{\text{Intensity at Q, assuming complete coherence}} = 0.85$$

For a line 470 Å long, = 0.78

[illegible] between the planes, which is what is measured on [illegible], is the complement of the angle between the plane normals c and b [illegible] i.e. $180^\circ - \alpha$ [illegible]

NOTE ON THE PRECESSION CAMERA

While the precession camera is much used in crystal structure investigation, there is one point concerned with the angles measured on the azimuthal circle which does not seem to have received much attention mainly because determination of triclinic cell dimensions on such a camera has not been very common. It has been assumed fairly generally that the angle measured, on the azimuthal circle, between two reciprocal lattice zero layers, is the appropriate reciprocal angle. This is true for symmetries of monoclinic or higher but is not true for triclinic systems, i.e. in general and, in fact, this angle is the complement of the appropriate real cell angle.

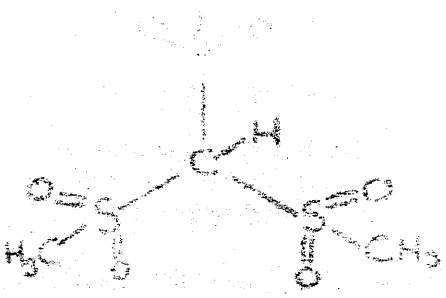
Thus the angle between $[a^* b^*]$ and $[a^* c^*]$ measured by rotation about a^* is $(180^\circ - \alpha)$.

Since $[a^* b^*] \perp c$ and $[a^* c^*] \perp b$, the dihedral angle between the planes, which is what is measured on the camera, is the complement of the angle between the plane normals c and b i.e. $180^\circ - \alpha$

In the monoclinic system $\alpha^* = 180^\circ - \alpha$ but this is not true for the general triclinic case.

PART II

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS (METHYLSULPHONYL) METHONE.

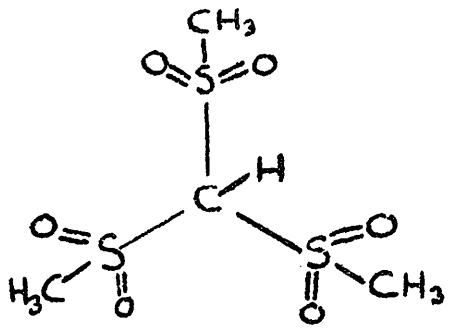


The configuration about the central carbon atom has been investigated by Gibson (1931) and Bohme & Marx (1941) by chemical methods. In both cases the results

INTRODUCTION

Before stating the reasons for the investigation it should be pointed out that an ethyl analogue of tris (methyl sulphonyl) methane exists and, for reasons that will become evident, the most logical way to undertake the structural determination might have been to determine the ethyl structure first. However, when the investigation started the ethyl compound had not been prepared and, in fact, crystals only became available towards the end of the work.

Tris (methyl sulphonyl) methane has the formula.



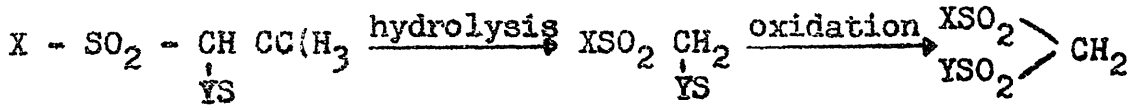
The conformation about the central carbon atom has been investigated by Gibson (1931) and Bohme & Marx (1941) by chemical methods. In both cases the results were inconclusive. Certain papers by Doering et al. (1955) had suggested that there might be some possibility that the compound might have a planar central configuration rather than a tetrahedral one but there was some doubt about

this. As confirmation of the suggestion of planarity was the fact that tris (methyl sulphonyl) methane (hereafter referred to as TMSM), is, although only sparingly soluble in water, a fairly strong acid. It was thought that the decrease in overlap due to a planar configuration would decrease the strength of the central C-H bond facilitating release of the hydrogen. Samen (1936, 1941, 1942, 1947) in his investigations on sulphones has reported that tris (methyl sulphonyl) methane has an acidity in aqueous solution indistinguishable from HCl.

PREPARATION ETC.

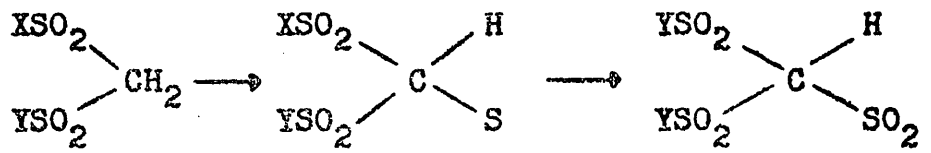
Gibson (1931) prepared the trisulphonyl methanes in order to investigate a suggestion of Frankland in his presidential address to the Chemical Society (1913) that 'optical activity can be preserved in an asymmetric system becoming ionised at the central atom'.

The various compounds were synthesised by the method of Brooker & Smiles (1926) involving the introduction of an alkyl thial group into a sulphonyl acetone, $RSO_2CH_2COCH_3$. It is apparently advisable to use a thiol sulphonic ester RSO_2S - Alk derived from the same sulphonic acid as there is evidence of interchange of RSO_2.



(I)

The disulphone (I) is recondensed with fresh sulphoxide and oxidised to the trisulphone.



The resulting trisulphones form salts very readily but optical activity was not detected. Although they are strong acids, the trisulphones are only slightly soluble in hot water and do not crystallize until a few drops of strong mineral acid are added to the solution.

The crystals will melt under pressure above 250°C but, in fact, start to sublime slightly below 200°C.

PRELIMINARY RESULTS

Crystals of TMSM from aqueous solution take the form of colourless needles elongated along the 3-fold axis. There is pronounced cleavage parallel to the needle axis which makes preparation of suitable specimens for x-ray investigation somewhat difficult. The usual result of trying to shorten a crystal is a collection of very fine

needles. The crystals also tend to have small satellite crystals attached whose removal is very difficult.

The various alkali metal and ammonium salts are stated by Fritzmeir (1949) to be monoclinic and isomorphous. This is true of the K, Rb, Tl and ammonium salts but not of the Cs salt. A goniometric investigation by Gibson and Carson (1949) showed this to be trigonal. This observation was confirmed during this investigation by means of a photograph.

Preliminary work by Abrahams and Speakman (1956) gave the following results for TMSM.

The Laue symmetry is $\bar{3}m$

In terms of hexagonal axes $a=b=12.90 \pm 0.02$ Å,

$c=9.53 \pm 0.02$ Å at 291°K.

The measured (flotation) density is 1.83 g/cc and six molecules in the unit cell would give a density of 1.82g/cc.

Space group Trigonal R 3c or R $\bar{3}$c C_{3v}^{6} or D_{3d}^{6}

Absent spectra: $hk\bar{1}$ for $-h+k+l \neq 3n$

$hh\bar{2}l$ for $l \neq 2n$

Stereochemical considerations make the centro-symmetrical space group R $\bar{3}$c, of twelve-fold multiplicity,

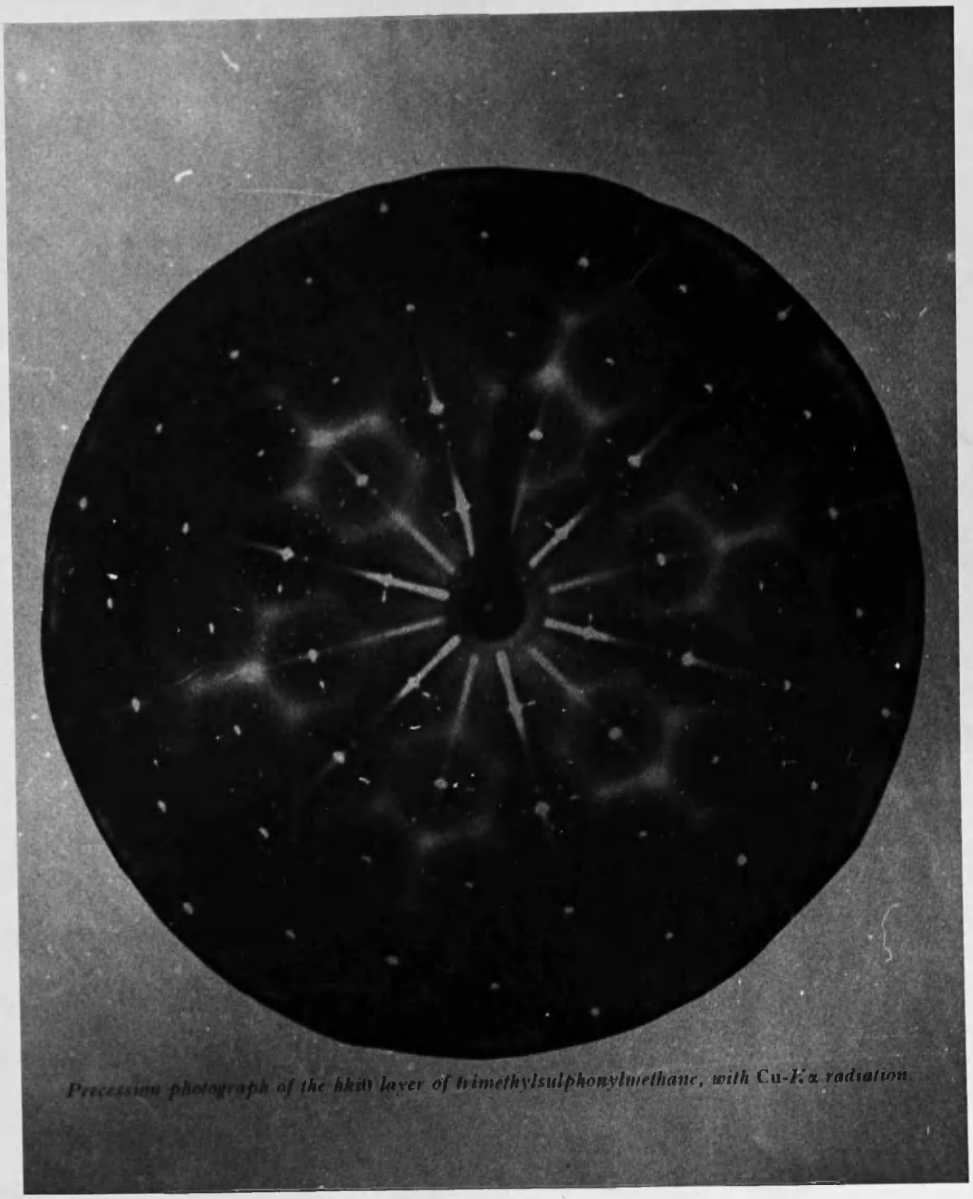
unlikely unless there is a statistical centre of symmetry based on half molecules in the twelve general positions.

The central carbon atom must lie on the 3-fold axis and there can be no indication as to whether the molecule is planar or pyramidal.

The most remarkable feature of this preliminary work was the reporting of strong diffuse scattering consisting of "diffuse spots around points in the reciprocal lattice forbidden by the space group obtained by consideration of the sharp (Bragg) reflexions. These diffuse spots are linked by intense diffuse ridges forming a honeycomb of diffuse hexagons around the sharp spots". (Figure 4) The diffuse reflection does not arise from thermal motion as it is still as pronounced at 78°K as at room temperature. The cell dimensions, for comparison, are $a=b=12.78\pm0.02$, $c=9.45\pm 0.03$ Å at 78°K.

A heat capacity and entropy measurement by Staveley & Davies (1956) indicates that there is no phase transition down to 22°K.

For the sake of completeness the cell dimensions and symmetry of tris (ethyl sulphonyl) methane will be recorded now, although it should be borne in mind that this was investigated at about the time when three-dimensional



Precession photograph of the hkiv layer of trimethylsulphonylmethane, with Cu-Kα radiation.

Figure 4.

work on TMSM was in progress.

Tris (ethyl sulphonyl) methane.

Trigonal, space group R $\bar{3}$c or R $\bar{3}$c

$a=b=14.92 \pm 0.02$ Å, $C=9.73 \pm 0.02$ Å

The most obvious difference from TMSM is in the total absence of any evidence of diffuse scattering. The lengthening of the a axis is to be expected and the similarity in length of the c axis to that of TMSM shows that there must be similarities in the packing of the two compounds.

As a point of interest, the density of the ethyl analogue is considerably less than that of the methyl, 1.55 g/cc as opposed to 1.82 g/cc respectively.

Leaving aside differences between the ethyl and methyl analogues which were not apparent when the investigation started, there were thus two reasons for interest in TMSM viz. the conformation of the central carbon atom and the unusual disorder.

TWO-DIMENSIONAL WORK ON TMSM

There was no electronic computing equipment available at Glasgow when this study commenced and hence a considerable amount of work was done in projection.

Initially it was decided to treat the space group as R3c and the structure as though ordered. Thus only the reflexions corresponding to R3c were estimated. It is difficult, in any case, to assign numerical values to broad diffuse reflexions, which would be required if it were treated as P3c1.

hk0 data were collected using photographic techniques and Cu K_α X-radiation by means of a Weissenberg camera and the Robertson (1943) multiple film technique. The data were later supplemented with data collected with Mo K_α X-radiation as the temperature factor is such that intensities are quite large at the limit for Cu X-radiation.

These data were placed on an approximate scale and an overall temperature factor estimated by the Wilson-Harker method. (Harker (1948); Wilson (1942)).

A Patterson projection on 001 gave rather approximate sulphur coordinates. The coordinates were not very accurate because two S-S vectors overlap due to the sulphurs being quite close to the glide planes.

PRELIMINARY COMMENTS ON THE DISORDER

While the diffuse scattering is very strong, it is confined quite accurately to layers in the reciprocal structure perpendicular to the c^* axis. There is no evidence for diffuse streaking parallel to c^*. The vertical dimension of the diffuse ridges can be seen to be equal to that of Bragg reflexions with quite high accuracy. (Figure 5). If one suspends consideration of the diffuse ridges which indicate a lack of regularity in the repeat distance parallel to a and considers only the local increase in diffuse intensity near the Bragg positions forbidden for R 3c, the space group is P3c1. The absence of streaking parallel to c^* indicates that the disorder is a two dimensional effect, the regularity of packing being maintained along the 3-fold axis. There is also no evidence for any deviation from exact maintenance of the C glide; there are no diffuse reflexions in $hoh\bar{1}$ for $l \neq 2n$. The effects could be explained by independent packing of stacks of molecules possessing 3c symmetry but having independent orientation (this could be rotation or inversion or both). On a regular basis this independence is possible for P3c1.

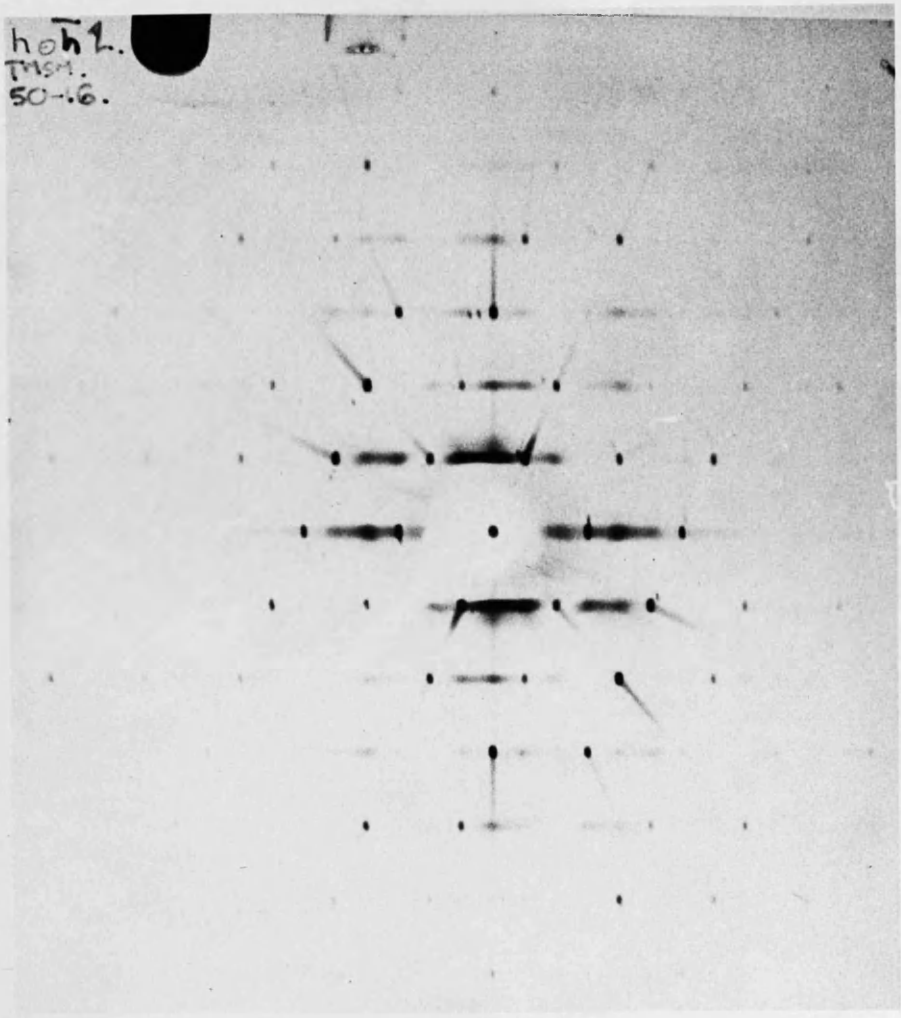


Figure 5.

No information could be deduced as to light atom positions.

However, by means of an electron density projection based on sulphur phases only, calculated with the help of Beevers-Lipson strips (1936), it was possible to deduce what appeared to be probable positions for the light atoms. The process of refinement was then commenced using difference maps. The projection is badly overlapped owing to two symmetry-related sulphur atoms being close to the glide plane and the process of refinement was laborious and slow. All calculations were done by hand. The discrepancy was slowly reduced from 40% with the sulphurs alone to about 25% with isotropic thermal parameters.

While, ordinarily, the introduction of anistropic thermal parameters at this stage of refinement would hardly be justified, especially for a compound with such a high melting point, it was felt that perhaps the disorder might be reflected in such parameters and refinement continued with anisotropy introduced. There did appear to be evidence of anistropy in the difference maps. However the refinement appeared to have concluded at a discrepancy of 18% and there were still some very large individual discrepancies, notably 900, which, although unobserved, invariably calculated fairly high. There was also some residual density in the difference maps which could not be correlated with a reasonable molecular

model. Consideration of structure factor graphs, after Bragg and Lipson (1936), also appeared to indicate that no structure consonant with reasonable molecular geometry would reduce the 900 discrepancy.

Two things were however observed; the largest residual amount of electron density was related to the sulphur atoms by means of a two-fold axis in projection and also the reflexions showing the largest discrepancies tended to have large imaginary parts in their structure factors. This suggested that possibly the structure was R $\bar{3}$c statistically. The actual assumption of centrosymmetry only increased R by a few percent but it was felt that, as the number of equations per parameter was rather low, any attempt to introduce a centre of symmetry (especially partially which appeared to give best agreement) was hardly justified.

In the cycles of refinement after anistropy was introduced the data had been supplemented by means of data collected with Mo k_{α} X-radiation and a precession camera. At this point there were 32 observed, independent reflexions. The number of parameters was 14 for the isotropic case and 22 for the anisotropic (the central carbon has no positional parameters, being at the cell origin, and its vibrations in projection must be isotropic).

The following coordinates were obtained from the cycle of refinement which gave the 18% discrepancy.

	x	y (2D)	x	y final 3D.
S	155	110	1525	1040
O_1	191	206	2062	2232
O_2	111	152	1410	1398
C_1	231	041	2213	0468
C_2	000	000	0000	0000

This set has some errors which must be attributed to overlap and a tendency to move towards the residual electron density. The atom attributed to an oxygen, O_1, is actually a carbon and vice versa. However no atom, apart from the central carbon, is at all well resolved in this projection.

It was then decided to consider the 010 projection. h0ℓ data were collected in the usual way with Cu K_α X-radiation and approximate z parameters calculated on a basis of expected bond lengths. The discrepancy for the h0ℓ data was 42% but the resulting electron density projection could not be interpreted readily either assuming a centre of symmetry or otherwise. Attempts were also made to interpret an electron density projection using phases determined by the sulphurs only but without any real success.

At this point it was decided that the best hope of a real solution would be by the use of three-dimensional methods.

THREE-DIMENSIONAL WORK ON TMSM

A small crystal was used such that absorption errors would be negligible and this was oriented along its c axis. Three-dimensional data were collected up to a value of $l = 11$ using MoK α-X-radiation and the Weissenberg technique. As the absorption of X-ray film for Mo radiation is small, the film packs were interleaved with 0.001" nickel foil. The "film-factor" at normal incidence was determined as 2.7. Intensities were estimated visually.

The data were corrected for Lorentz-polarisation and Tunell inclination factors (1939) by hand. The various layers of structure amplitudes were then correlated and placed on the scale of hk0 by the use of the hk0, h0l and h1l data. Some reflexions, missing because the camera design prevented their reaching the films, were also added from h0l and h1l The h0l and h1l data were collected by means of timed series taken on a precession camera with MoKα X-radiation produced by a stabilised X-ray generator.

The limit of $\sin\theta/\lambda$ was ca. 0.850 A^{o-1}, which corresponds, according to Bragg & West (1930), to a limit of resolution of 0.35 A^{o}.

THREE-DIMENSIONAL PATTERSON FUNCTION

(a) Calculation

The Patterson function was evaluated treating the cell as triclinic after generating the twelve-fold set of observed intensities.

The generation was carried out by hand and there appear to have been some errors which manifested themselves as slight deviations from the true symmetry in the Patterson function. However these deviations did not affect the conclusions.

The actual process was to carry out a one-dimensional summation for $\frac{1}{}$ and then to set the coefficients into X-RAC. It appears likely that there were also some slight errors in preparing the computer input for the one-dimensional summation and the input to X-RAC. X-RAC was made available by kind permission of Professor R. Pepinsky. The television screen output was contoured at 12 arbitrary levels and a grid was superimposed in 20ths of a and b. Sections were calculated perpendicular to c at intervals of $\frac{1}{30}$.

(b) Interpretation of Patterson Function

The xy coordinates of the sulphur atom were readily deduced from the sections at $z=0$ and $z=\frac{1}{2}$ as approximately

0.157, 0.107. In space group R3C the origin is defined only as being on the 3-fold axis and hence the z-coordinate of one atom can be chosen as zero. This value was assigned to the z-coordinate of the sulphur atom.

Still assuming R3c, a partial solution for the other atoms can be obtained but a true explanation for all the peaks is not given. However one atomic position, at least, is obvious. The section at z=0 has a hexagon of peaks surrounding the origin peak. The heights of these peaks are comparable with S-S interactions. The section can be seen in figure 6).

The peaks can be interpreted as each being due to two overlapping S-O vectors, the height of an S-O peak being about half that of an S-S. This means that there is an oxygen atom having the same z parameter, approximately, as the sulphur atoms. Although the sections at z = 0 and z = $\frac{1}{2}$ are both Harker sections, it is not possible to derive any definite information about the light atoms except that the coordinates of the oxygen atom just mentioned are compatible with the vector pattern. It is possible that the peak height for two S-C vectors might also account for the observed value but the vector distance is 1.4 Å and one would expect an S-C vector to be ca 1.8 Å.

The major problem in interpretation lies in sections z = 9/30, z = 10/30. These are shown in (figures 7,8).

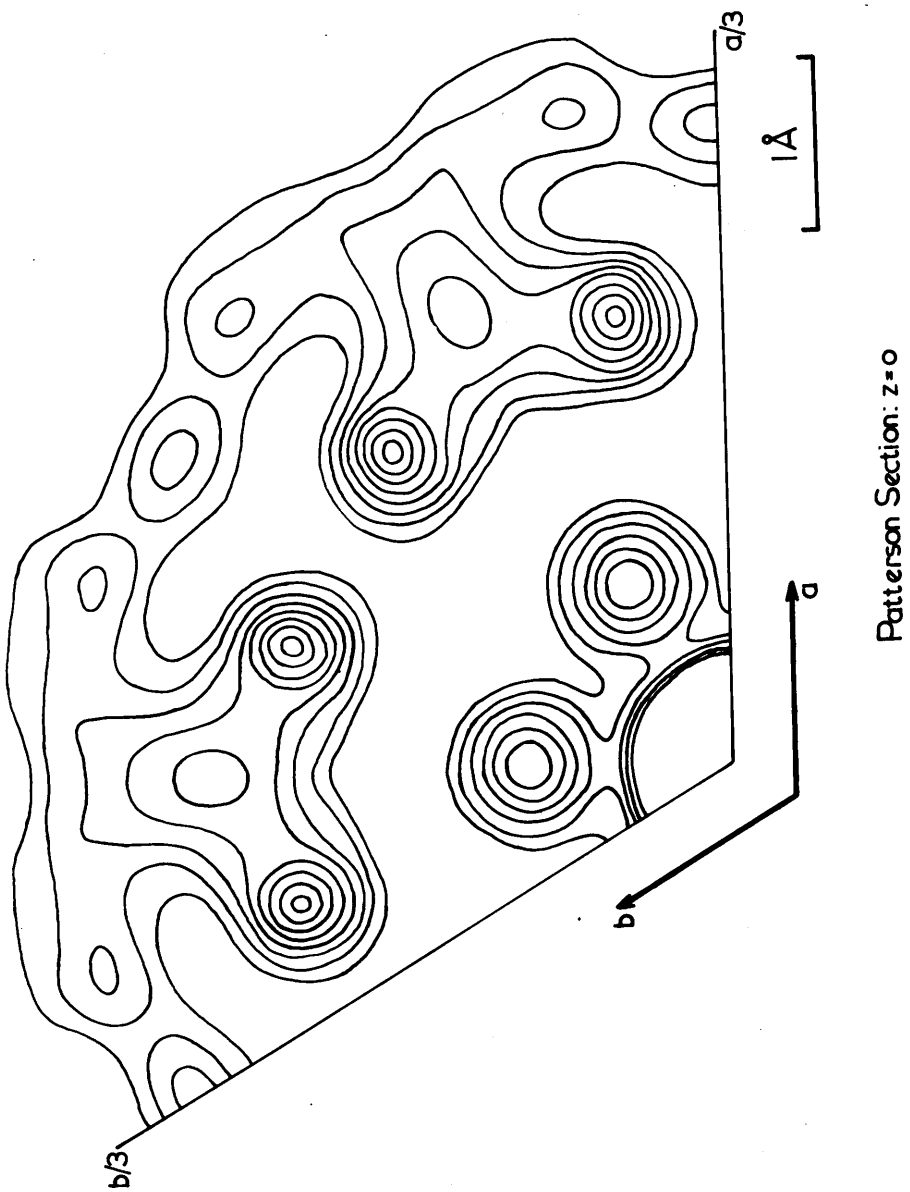


Figure 6.

Figure 8.

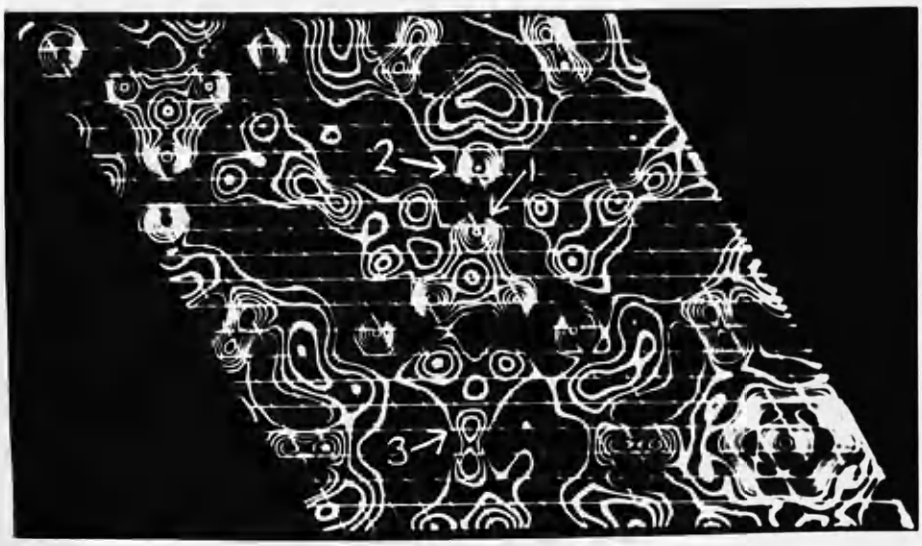
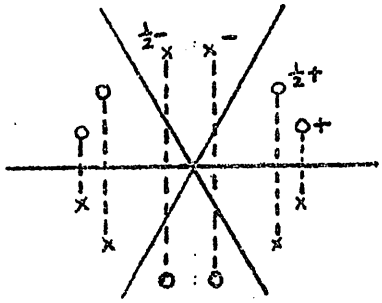


Figure 7.

When the Patterson was first calculated, an attempt was made to settle the question of whether or not the space-group was R $\bar{3}$ c by searching for planar concentrations of vectors, following Buerger (1950). If the space group is R $\bar{3}$ c there should be such a concentration on the plane x2xz and, in fact, if one considers section z=5/30 one does see a series of large peaks on the intersections of such planes with the section. There are six large peaks, nearly as large as S-S peaks on the section z=0. However such peaks arise from the interactions shown in the diagram and there should be 9 equal peaks of double weight. The peaks are marked



1, 2, and 3 in figure 7 and it will be seen that peak 3 is considerably smaller than peaks 1 and 2. Moreover there are other double weight peaks if the space group is R $\bar{3}$c, notably on section z =10/30 if ½ + z = 5/30, where there should be double weight peaks at

$y-x, x, 2\bar{z}$; $y-x$; $y\ \bar{2}z$; $\bar{y}, x-y, \bar{2}z$; $x, x-y, \bar{2}z$; $x\ y\ \bar{2}z$; $\bar{y}\ \bar{x}, \bar{2}z$

and single weight peaks at

$\bar{2}x, \bar{2}y, \bar{2}z$; $2y, 2x, \bar{2}z$; $2y, 2y-2x, \bar{2}z$; $\bar{2}x, 2y-2x; \bar{2}z$; $2x-2y, 2x, \bar{2}z$; $2x-2y, \bar{2}y, \bar{2}z$

The appropriate peaks are there; marked for typical single and double weight peaks in Figure 8, but their heights are only about half that which would be expected.

On the section, $z = 0$, there should be, for space groups R 3c and R $\bar{3}$c, 12 peaks due to the various triangles of sulphur atoms (related by the 3-fold axis). The only difference between the space-groups is that for R $\bar{3}$c the peaks are double-weight. The peaks which correspond to S-S interactions have heights of 8 contours, so that a double-weight S-S peak is of height 8 rather than ca.4 which is the actual height on non-zero sections.

The first assumption made on the basis of peak heights, was that the peaks were due not to centrosymmetrical S-S interactions but to vectors between sulphur and light atoms. This is supported by the fact that the vector distance to the closest-in peaks is 1.8 Å; the length of an S-C bond. However if carbon atoms are placed at such positions and oxygen atoms at positions indicated by the vectors at $z = 0$, the molecular geometry is rather strange, some bond angles being less than 90°, notably the C_oSC angle where Co is the central carbon atom placed at any reasonable height.

By what is now realised to be a rather cavalier disregard of certain peaks, a partial interpretation on a

basis of R 3c was attained and an attempt was made to refine this by least-squares techniques. However the discrepancy index was never reduced below 40% and the resulting bond angles after refinement were most unlikely. The final coordinates indicated that there had been a tendency for the light atoms to move in such a fashion as to give some electron density near positions related to the sulphur atom by a centre of symmetry. Also the refined z-coordinate of the central carbon atom seemed greater than would be expected.

FURTHER WORK ON PATTERSON, BASED ON A PARTIAL APPROACH TO R $\bar{3}$c.

It has become apparent that some explanation of the disorder would be required if any real hope of solving the Patterson was to be entertained.

As a first approach, the triangle of sulphur atoms related by the 3-fold axis was used as an image-seeking function. This method led definitely to the conclusion that there was some density at the centrosymmetrical position.

The most likely explanation now appeared to be that, in what one may call 'the average structure' in the unit defined by the stated cell lengths, there must be some partial approach to centrosymmetry. In other words that sites

related by a centre of symmetry were filled statistically but in such a manner that the occupancy was not equal.

If the fraction in one site is r the fraction in the other site must be 1- r.

Then the height of a peak on section z =0 will be proportional to $r^2 + (1-r)^2$ and a peak on $z_{Sulphur} + \frac{1}{2}$ i.e. z =10/30 will be proportional to 2r(1-r).

If r=0.5 these heights will be equal.

The actual ratio between the peak heights is somewhat doubtful because the zero value of the Patterson is unknown; the author was not present when it was calculated and was unable to find out whether or not an origin term had been included or how the zero of contours had been adjusted. Assuming the heights are accurate and that the $z + \frac{1}{2}$ peaks are only half the height of those at z = 0, one arrives at a value of r =0.78. The large uncontoured areas suggest that the peak height ratio will be less than 2 and thus r must lie somewhere between 0.78 and 0.5.

In agreement with this is the fact that, as stated earlier, the local intensification of the disorder streaking suggests that there must be a partial approach to P 3Cl. If 6 molecules are placed in P3Cl, with pairs of molecules at 000, $\frac{1}{3}\ \frac{2}{3}\ \frac{2}{3}$, $\frac{2}{3}\ \frac{1}{3}\ \frac{1}{3}$ and allowing the only difference of

orientation to be that required by a centre of symmetry, two pairs of molecules must be oriented similarly. If such an orientation is averaged over all three sites, r then equals 0.667.

On a basis of r = 2/3, a set of coordinates could be derived. There was however a degree of uncertainty due to the overlap of peaks. To obtain confirmation of the partial approach to $R\bar{3}c$ and also to attempt to find better information about light atom positions, it was decided to try Fourier methods.

FOURIER METHODS

To calculate electron density functions by Fourier methods it was necessary to write the program given in the introduction, in order to be able to use Rollet's Fourier program for the Glasgow computer 'Deuce'.

Structure factors were calculated based only on S atoms in the R 3c positions using Rollet's program and the 'Deuce' computer. The discrepancy, on observed reflexions was 44%.

After generating the three-fold set of structure factors necessary, the electron density was evaluated over a volume large enough to contain the asymmetric unit of R 3c.

The electron density map showed the sulphur atom and what appeared to be fairly reasonable positions for the attached light atoms. Agreement with the Patterson function appeared satisfactory. The section through the sulphur atom is given in figure 9. The electron density at the centre of the sulphur atom is $28e/A^{o3}$.

What was very interesting, in view of the fact that it was thought that the structure would be represented by a partial approach to R $\bar{3}$c, was the appearance of a large peak with x and y coordinates related to the sulphur atom by means of a two-fold rotation and at a distance corresponding to the that appropriate from the Patterson map. This is shown in figure 10 . The peak height is $5e/A^{o3}$, larger than any of the light atom peaks, and the area on the section is larger than that of any of the light atoms. The area is, in fact, comparable with that of a sulphur atom.

To establish that this peak was not fortuitous and also to check the light atom positions, a few cycles of refinement were carried out using an ordered R3c structure leaving out this peak.

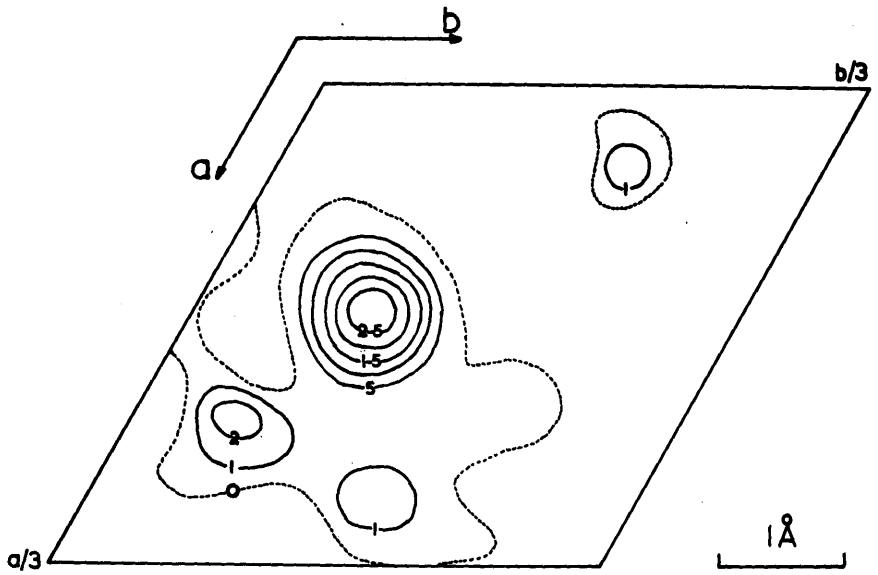


Figure 9.

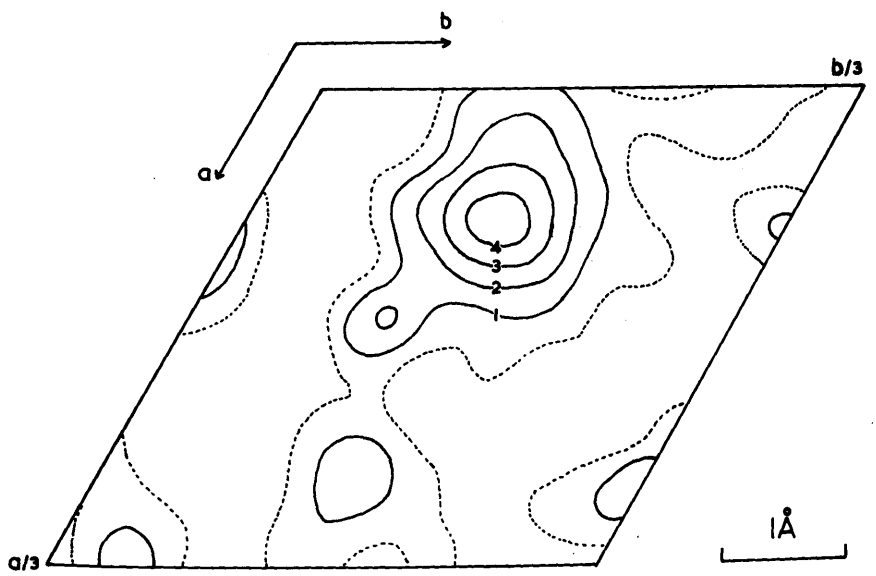


Figure 10.

THREE DIMENSIONAL REFINEMENT

(a) Ordered structure

Using Rollet's least-squares program and the 'Deuce' computer, four cycles of refinement reduced the discrepancy to 32%, at which point the coordinates began to oscillate. Calculation of bond lengths and angles revealed that the $C_{Central}$ - S distance had increased to 2Å, rather than the expected 1.8 Å and S-C_{methyl} had decreased to 1.4 Å. These results are comparable with the previous attempt at three-dimensional refinement.

A difference synthesis revealed that the density at the large peak in the first electron density map was still present and also that large difference densities existed. It was also suspicious that some of the scale factors for the independently collected layers diverged greatly from those originally assigned if agreement was to be optimum.

(b) Refinement on a basis of 2:1 occupancy ratio

Assuming now that there was a partial approach to centrosymmetry, structure factors were calculated for a centro-symmetrical coordinate distribution based on the first electron density map and various occupancy ratios. A ratio of 2:1 gave the best discrepancy; 25%.

A second difference map was now calculated. Better values for the sulphur and oxygen coordinates were readily obtained. Careful examination revealed also that the first electron density map had given what were, in two cases, essentially the means of the partially related positions. The reason for this is the close approach of one 2/3 molecule and the centrosymmetrically related ⅓ molecule of the one related to the first by a glide plane. The position is shown in Figure 11 . The difference map indicated that the two methyl carbons were sufficiently far apart, ca. 1 Å, to be refined successfully but the two central carbon atoms were very close, in fact very near the limit of resolution of ca. 0.35 Å. This close approach and refinement to the mean of positions explains why the central carbon atom moved so far from the sulphurs.

Structure factors were now calculated, based on the difference map coordinates giving a discrepancy of 21.4%. After re-checking layer scale factors the discrepancy was reduced to 18%. The scale factors which had been used were deduced from the refinement on an ordered basis and the new scale factors were nearer those obtained by correlation with crossing series although not absolutely identical. A small deviation from these cross-correlated scale factors can be justified because the number of common reflexions on crossing series is small. In any case the deviations are small.

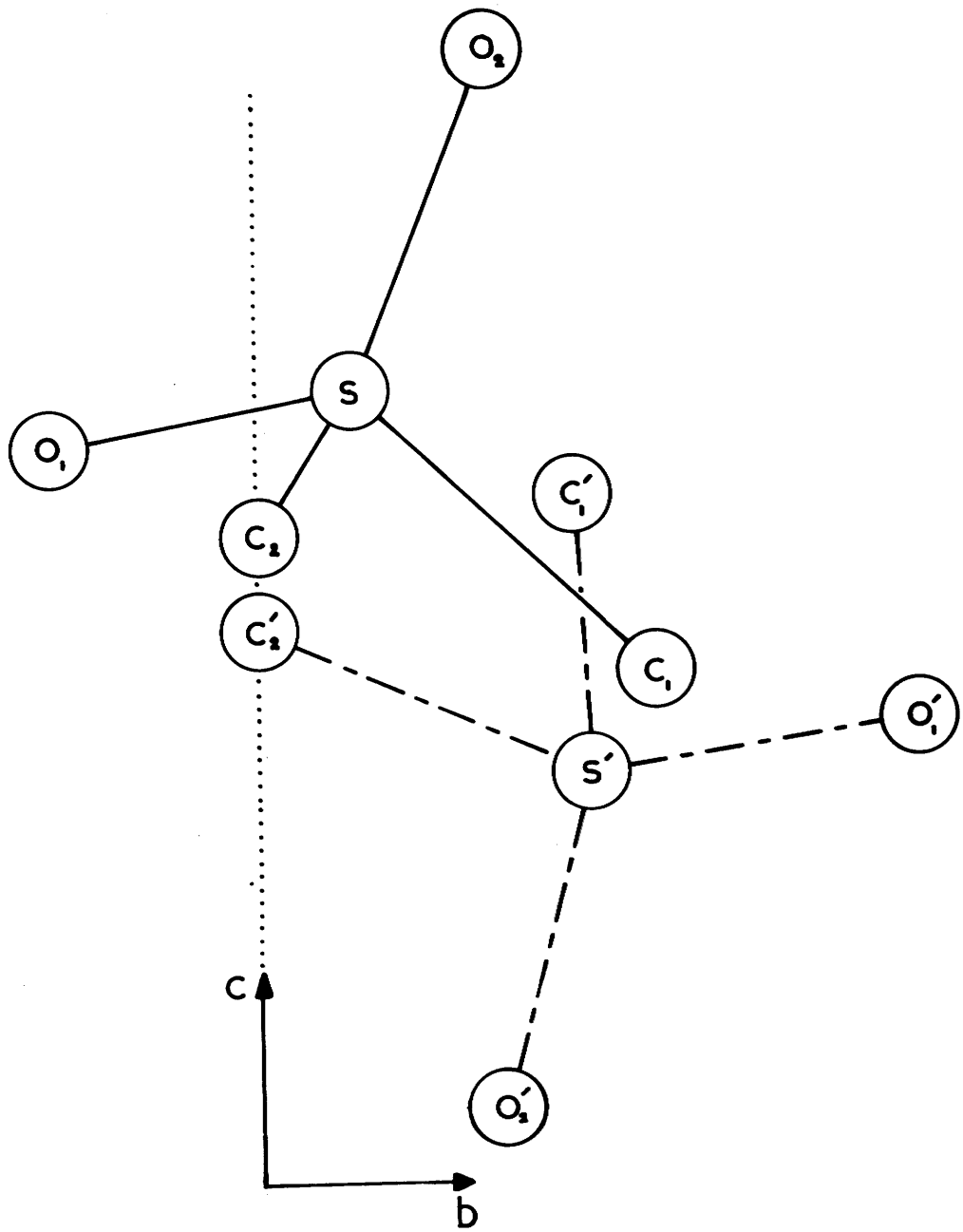


Figure 11.

(c) Least squares refinement on 2:1 basis

The Hollet least squares program for 'Deuce' uses a block diagonal approach. The 10 x 10 full matrix for each atom is reduced to a 3 x 3 matrix for coordinates, a 6 x 6 matrix for anisotropic thermal parameters and a 2 x 2 matrix correlating the overall scale and temperature factors. It is not possible to refine directly isotropically.

The weighting scheme used was $\sqrt{\omega} = 1$ for $F_{obs} < 8\,F_{Minimum}$ and $\sqrt{\omega} = \frac{8\,F_{Minimum}}{F_{obs}}$ for $F_{obs} > 8\,F_{Min.}$

Approximate isotropic thermal parameter shifts were calculated from the anisotropic ones given by the program. Although the two related sets of atoms were treated independently in the program, the given shifts were averaged on a 2:1 weighting and the centrosymmetric coordinate relationship maintained.

After four cycles of least squares refinement the discrepancy was reduced to 10.2% and the weighted sum of squares of differences was reduced from 572 to 256 This is based on observed reflexions only.

In the last two cycles of refinement it began to be apparent that the program was tending to decrease the temperature factor of the $\frac{1}{2}$ atom relative to that of the $\frac{1}{2}$

atom. It was realised that this was probably symptomatic of the fact the occupancy ratio was other 2:1 but this ratio cannot be refined by Rollet's program.

(d) Refinement of occupancy ratio

It would have been possible to experiment with various occupancy ratios to find that which would give the best discrepancy but it was felt that a fairer approach would be to refine the ratio in conjunction with the other parameters by least-squares.

As an experiment two other ratios were tried at this point; 1:0 (i.e. R3c) which gave a discrepancy of 27.1% with bad individual agreement, and 1:1 (i.e. R$\bar{3}$c exactly) which gave a discrepancy of 11.6%.

At this point the author informed Dr. S. C. Abrahams of the results as they then stood and he kindly offered to refine the occupancy factors and cell parameters on an IBM 7090 computer at Bell Telephone Labs.

Initially, as a check, the atomic occupancy factors were allowed to vary individually but, after 3 cycles of refinement, all occupancy factors were equal to that of the sulphur atom within their limits of error. The occupancy factor was then 0.6108 ± 0.0076. Two further cycles of

refinement were carried out, holding the occupancy factor constant, which gave a final discrepancy, on observed reflexions, of 9.1%.

The final list of observed and calculated structure factors is given as table 1 .

The central carbon atoms were slightly more than 0.4 Å apart at the start of least-squares refinement and they moved somewhat closer in the process of refinement. As a check that the final positions were correct and that they had not stayed in one place due to resolution troubles, the experiment of moving them apart and refining only them was tried. The Rollet program which was used tends to overshift atoms in special positions and thus one quarter of the indicated shifts was applied. The indicated direction of shift was never in doubt. The experiment commenced with the atoms 0.85 Å apart which would certainly allow them to refine to a planar configuration if this was correct but, after three cycles of least-squares refinement with quarter shifts, the atoms had moved to 0.44 Å apart. The discrepancy changed from 12.1% at 0.85 Å to 9.4% at 0.44 Å. The final least-squares coordinate of the central carbon atom with the higher occupancy factor was 0.26851 and, in this experiment, after three cycles, the coordinate was 0.27300 with an indicated

further shift towards the lower value. Thus it would appear that later observations on the molecular conformation can be taken as correct.

[illegible] .2c651 [illegible]

[illegible] bond lengths are -

[illegible]	1.434 ± .0195	Å
[illegible]	1.438 ± .013	Å
[illegible]	1.735 ± .017	Å
[illegible]	1.439 ± .009	Å

[illegible] bond angles are -

[illegible]	119.4 ± 1.9°	$C_2\hat{S}C_1$	104.9 ± [illegible]°
[illegible]	110.9 ± 0.4°	$O_2\hat{S}C_1$	111.1 ± [illegible]°
$C_2\hat{S}C_1$	107.2 ± 1.4°	$O_1\hat{S}C_1$	106.7 ± [illegible]°
$C_2\hat{S}O_2$	106.8 ± 1.4°		

The nomenclature of atoms is shown in figure 1 [illegible] bond lengths and figure 13 which shows

MOLECULAR STRUCTURE

The final, least-squares-adjusted, parameters are.

	x	y	z	Standard deviations	σ(x)	σ(y)	σ(z)
S	.15250	.10402	.32774		.00035	.00033	.00055
O_1	.22125	.04676	.30606		.00140	.00141	.00136
O_2	.14096	.13975	.46721		.00124	.00132	.00118
C_1	.20621	.22324	.21213		.00165	.00156	.00144
C_2	00000	00000	.26851		00000	00000	.00264

The appropriate bond lengths are -

$S-O_1$ $1.424 \pm .0198$ Å

$S-O_2$ $1.438 \pm .013$ Å

$S-C_1$ $1.735 \pm .017$ Å

$S-C_2$ $1.829 \pm .009$ Å

The bond angles are -

$O_1 \hat{S} O_2$ $119.4 \pm 1.9^\circ$ $C_2 \hat{S} C_1$ $104.9 \pm 1.1^\circ$

$S' \hat{C} S$ $110.9 \pm 0.4^\circ$ $O_2 \hat{S} C_1$ $111.1 \pm 1.9^\circ$

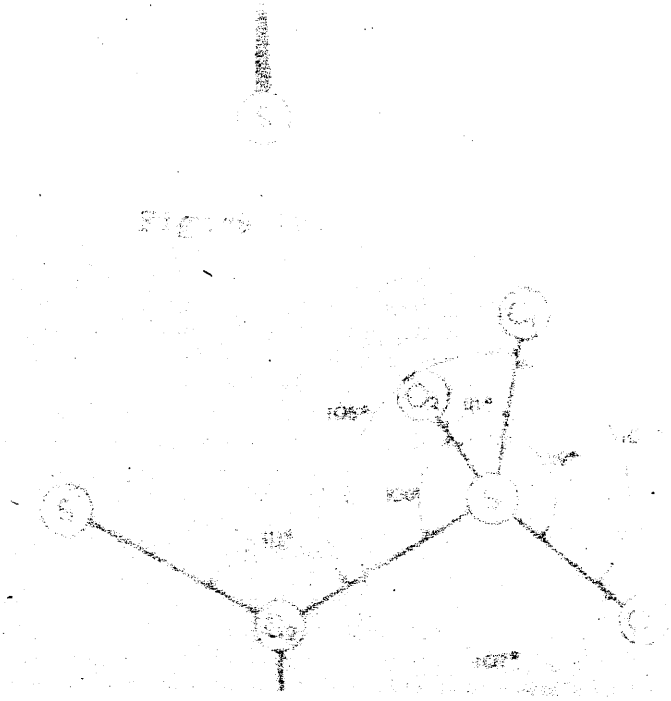
$C_2 \hat{S} O_1$ $107.2 \pm 1.4^\circ$ $O_1 \hat{S} C_1$ $106.7 \pm 1.8^\circ$

$C_2 \hat{S} O_2$ $106.0 \pm 1.4^\circ$

The nomenclature of atoms is shown in figure 12 which shows the bond lengths and figure 13 which shows the bond angles.

The thermal parameters are as follows:-

Atom	B ($Å^2$)	$\sigma(B)$ ($Å^2$)
S	1.923	0.076
O_1	3.585	0.255
O_2	3.058	0.234
C_1	2.425	0.288
C_2	2.627	0.366



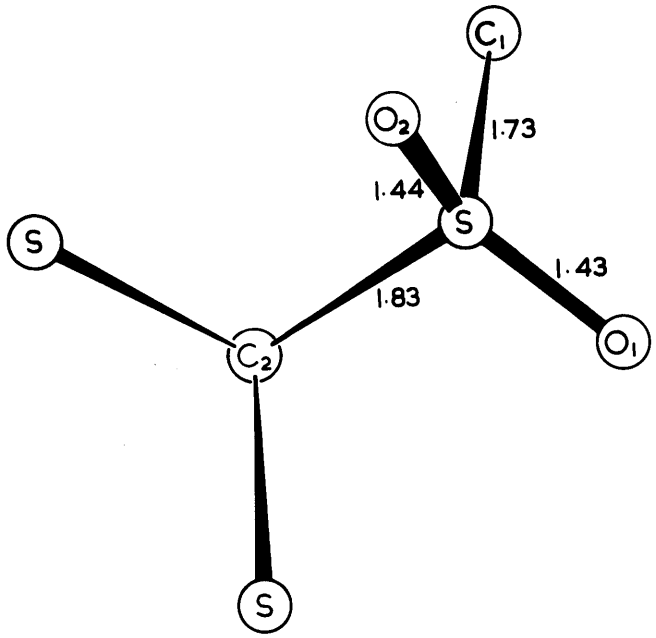


Figure 12.

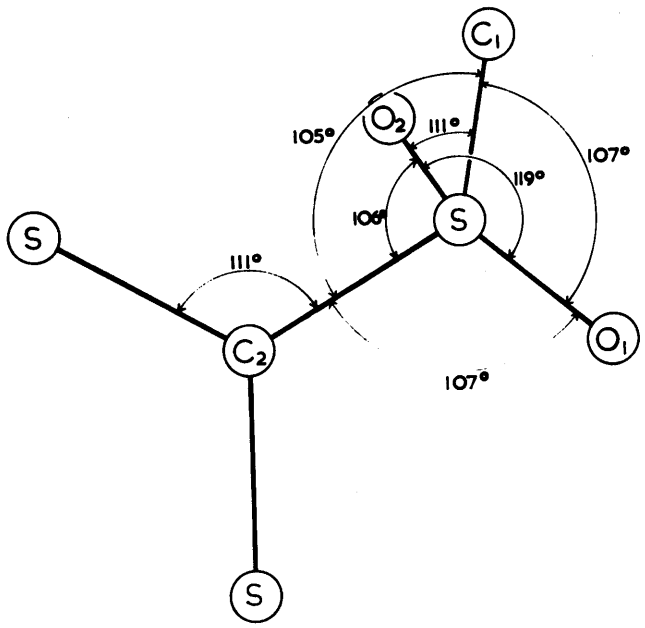


Figure 13.

COMMENTS ON STRUCTURE

(a) It is evident that the conformation at the central carbon is pyramidal rather than planar. The angle is slightly flattened from the tetrahedral angle of 109.45°. The difference is over three times the standard deviation of the angle and is probably significant (95% probable at least).

(b) The $\hat{OSO}$ angle has diverged greatly from a tetratedral angle and even although the standard deviation of the angle is fairly large the difference is definitely significant (99.98% probable). This is consistent with other studies where angles from 113° to 130° have been recorded. The angle is not significantly different from that in SO_2 ; $120^{\circ} \pm 2^{\circ}$.

(c) The other angles are fairly close to the tetrahedral angle, although some differences from it, notably those of $C_2\hat{S}C$ and $C_2\hat{S}O_1$, are over twice the standard deviation.

(d) The S-O distances are not significantly different and their average, 1.432, is very much what has been observed in similar compounds. This distance in dimethyl sulphone, by electron diffraction methods is 1.43 ± 0.02 Å as quoted by Allan and Sutton (1950). It is notable that the tendency for sulphone S-O lengths to remain constant at 1.43 Å and for the $\hat{OSO}$ to be greater than tetrahedral in many different compounds is maintained here.

(e) The distance $S-C_2$ can be compared with that in dimethyl sulphone in the above study 1.83 as against 1.80 $\pm$.002 Å.

(f) The distance $S-C_1$ is rather less than that in dimethyl sulphone. The difference 0.06 is probably significant given the calculated standard deviation of 0.017 Å. The standard deviation of the difference between these two measurements is however ca. 0.03 Å and the difference is only twice this value.

If the structure had been ordered, the standard deviations of lengths and angles might well have been less but the above values are based on an average structure which is not an exact representation of the situation in the crystal and are thus somewhat higher than would be expected in an ordered structure refined to the same level.

(g) It is possibly interesting to compare these values with those obtained by Hoogsteen (1957) and given in his thesis but not otherwise published. Hoogsteen studied the tris (methyl sulphonyl) methyl ion as its ammonium salt. It is monoclinic and no molecular symmetry is required but the resulting average lengths and angles are as follows:-

SO_1 = 1.43

$S-C_{Methyl}$ = 1.78

$S-C_{Central}$ = 1.70

As it is an ion the lengths are probably not directly comparable but there is a fair measure of agreement except for $S\text{-}C_{Central}$. Although the standard deviation of the only variable parameter of the central carbon atom in TMSM is higher than all other standard deviations of position, the carbon position does not greatly effect the length and, in fact, if the carbon were at the same height as the sulphur the length would still be 1.74 Å.

The average O SO angle found by Hoogsteen was 117°.

MOLECULAR STRUCTURE AND PACKING

(a) Single molecule

Given the bond lengths and angles observed it can be seen that the molecule is arranged in a manner which is probably the most logical one. It is quite evident if a space-filling molecular model of the Stuart or Catalin type is constructed. What actually happens is that the bulky methyl groups are on that side of the molecule where there is most room and one set of the smaller oxygen atoms is on the other side. The model seems to indicate that there would be a considerable barrier to free rotation of the sulphur atoms and attached groups and the position adopted is one of minimum energy. The situation would not be as favourable sterically if the methyl carbon (C_1) and oxygen (O_2) were interchanged. The third possibility which might arise would be the interchange of the methyl carbon (C_1) and oxygen (O_1) i.e. to bring the methyls into more or less the same plane as the sulphurs. This also would be unfavourable sterically as can be seen when one considers that the distance O_1 - S (figure 14) is only 3.32 Å. The more relevant intra-molecular distances are given in the diagram.

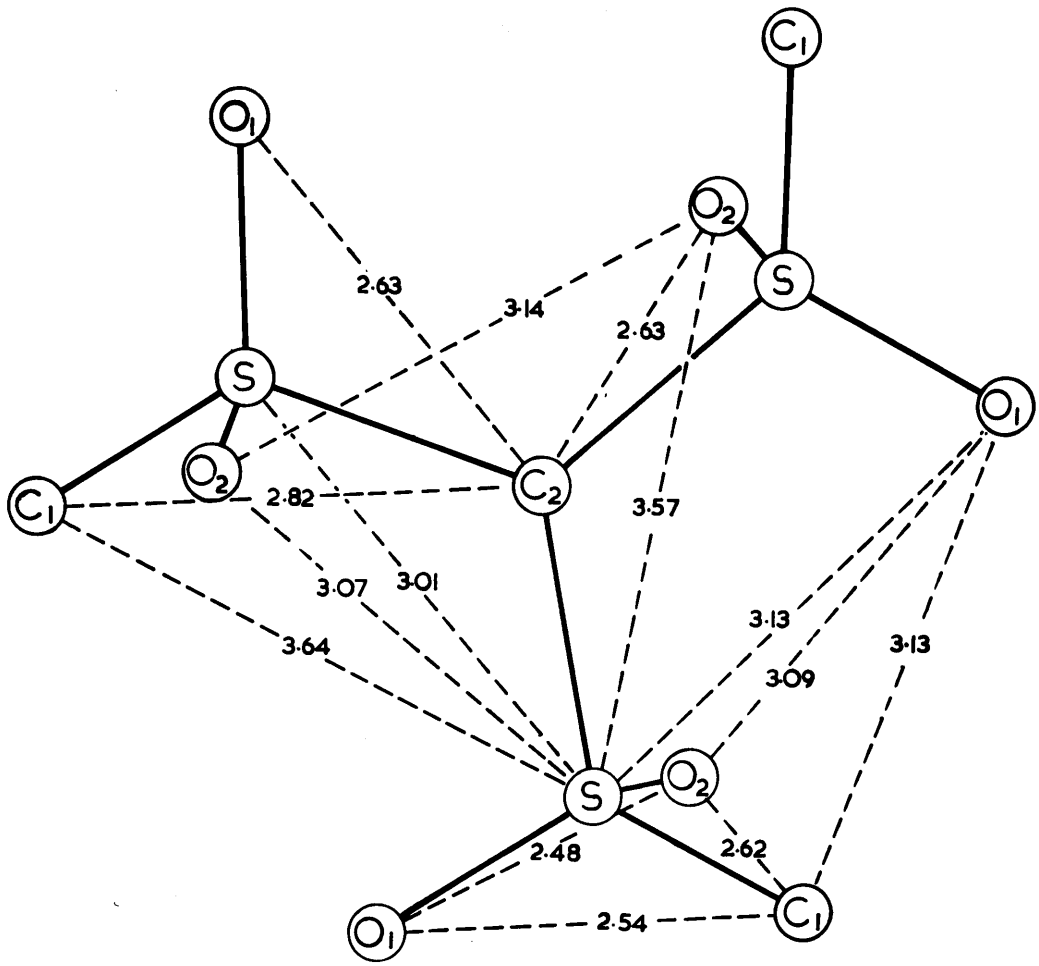

C1
O1
O2
S
2·63
3·14
2·63
S
O1
O2
C2
C1
2·82
3·57
3·07
3·01
3·64
3·13
3·09
3·13
S
O2
2·48
2·62
O1
2·54
C1

Figure 14.

(b) Molecular stacking along 3-fold axes

It would seem relevant to discuss packing along a 3-fold axis separately from the overall packing because, first, there is probably no disorder involved in this packing and second, the molecules appear to interact most strongly in this sense as evidenced by the ready cleavage parallel to the 3-fold axis.

The space group does not require any definite orientation of one molecule with respect to the one $\frac{1}{2}c$ above. The actual angle chosen would appear to be governed by packing considerations. If the molecule has a large dipole moment, as seems likely, there presumably is an attractive force between the molecules and the configuration adopted seems to allow them to be as close as possible. In fact, in the molecule itself and in the vertical stacks, space is utilised rather efficiently, as is shown by the comparatively high density of 1.82 g./cc. Dimethyl sulphone, for comparison, has a density of 1.42 g./cc.

The relevant distances are shown in figures 15, 15a.

The dipole moment is estimated as follows.

The dipole moment of $(CH_3)_2$ S is 1.40 D.

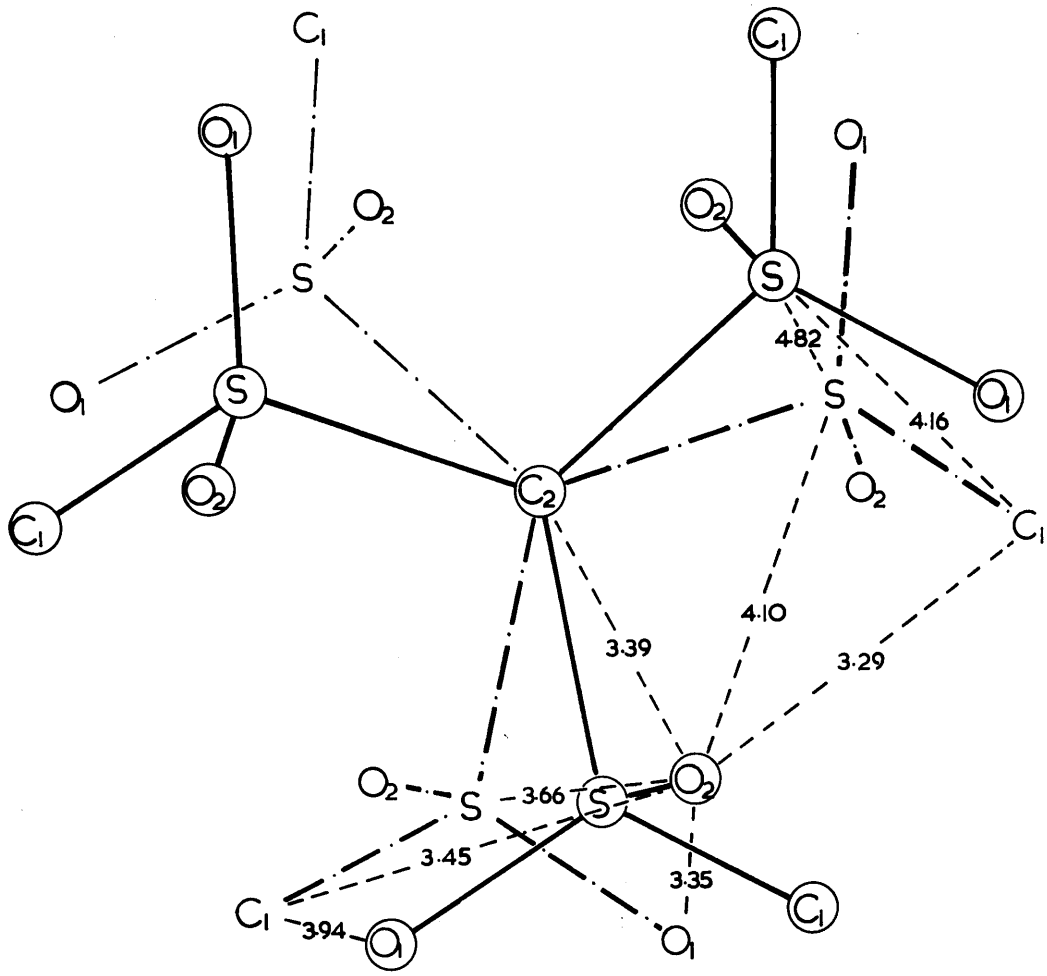

Cl
O1
O2
S
O1
S
Cl
O2
C2
Cl
O2
S
O1
S
Cl
4·82
4·16
O2
4·10
3·39
3·29
O2
S
3·66
S
O2
3·45
3·35
Cl
3·94
O1
O1
Cl

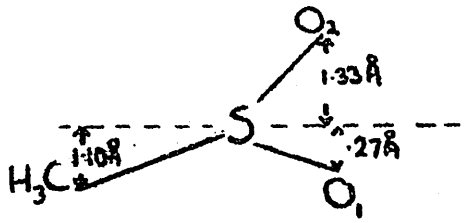
Figure 15.

Treating the resultant dipole as the sum of the dipole vectors along H_3C-S, this means, if the angle C-S-C is ca. 109°, that the H_3C-S dipole is + 1.2D along the bond.

In $(CH_3)_2\ SO_2$ the dipole moment is 4.41 D in the same sense. Thus the SO_2 dipole is ca. 3.0 D and, if the O-S-O angle is 120°, the S - O dipole is 3.0 D.

In the TMSM molecule, the dipole components in any direction but along the 3-fold axis will cancel.

The situation at each sulphur, neglecting the $HC_{Central}$ - S dipoles is as follows.



Vector components of dipoles are H_3C-S 0.17 ↑

O_1- S 0.46 ↓

O_2- S 2.79 ↑

Σ = 3.10D ↑

Thus the total molecular dipole should be ca. 9 D, if one can validly separate the dipole moments along different bonds as in this calculation.

The tight packing vertically of molecules with a large dipole in some ways resembles the situation in metaldehyde as described by Pauling & Carpenter (1936).

DISORDER

As previously mentioned, the disorder streaking is confined, quite exactly to layers perpendicular to c^* and there is no deviation from the glide plane absences. Thus the disorder must be associated with the packing of, what one might call, 'stacks' of molecules which are themselves ordered in the c direction.

The model used for the least-squares refinement postulates an arrangement whereby these stacks have both possible orientations required to give, on average, an approach to a centre of symmetry but the choice of a given orientation is random. The actual positions of the stacks are as required for placing on an ordered hexagonal lattice on the 001 plane. The actual repeat distance a is probably decided by its being the minimum value for a random arrangement. However, in the refined structure, the coordinate required for a centro-symmetrical placing is not zero. If a molecule is inverted it is also translated. This translation would seem to be required by packing considerations as two molecules at the same height but related by a centre of symmetry would be too close to each other. The fact that completely random arrangement of ordered stacks is neither apparently reasonable or suggested by the average structure indicates that environment of a molecule is conditioned by the orientation of that molecule.

Since a molecule of TMSM has a three-fold axis it does not seem unlikely that there will be a tendency for its environment to retain the three-fold axis. There might be a tendency for a molecule to have at least its three nearest neighbours oriented similarly. This analysis is in agreement with the a tual nature of the diffuse scattering which has a regular appearance and is consistent with the idea that such scattering is explicable by short range order.

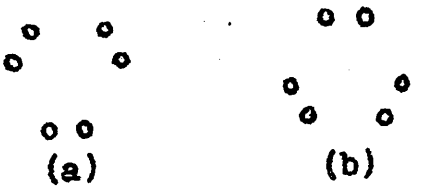
Taylor, Hinde and Lipson (1951) investigated the cubic random alloy Cu_3 Au by the use of an optical diffractometer and showed the tendency for diffuse reflexions to align themselves as short range order was introduced. They used several hundred atoms in their masks and, in the case of TMSM, the punching of masks with similar numbers of molecules would have been impossible in any reasonable time. With the available equipment for punching masks, insufficient molecules for randomness to have any real meaning could be punched. It was realised, after some work in a different fashion, that it would be possible to show the lining up of diffuse spots in the given crystal system but transforms produced from such a mask would not be directly comparable with the X-ray photographs in even a semi-quantitative fashion.

The approach which was actually used was to attempt to find a model based on a small number of molecules which

would reproduce the observed diffuse scattering.

The model would, in the nature of things, have only short range order but no true repeat unit. This description would be valid for the whole crystal and thus the disadvantage of the small number of molecules representable on a mask could be turned to advantage. It was also considered that such a model would allow testing various types of short range order.

In the work described below masks were punched in black plastic film on a scale of 0.83 cm. to one cell division. The drawings from which the masks were made had a scale of 10 cm to a cell division and a pantograph punch reduced this by a factor of 12. Only the sulphur atoms were punched and two glide related molecules were represented by their projection on 001 as it was decided to consider the hk0 photograph for comparison. The holes in the mask were 0.5 mm in diameter. The average structure allows two centrosymmentrically related orientations, and these were represented thus:-



(a) (b)

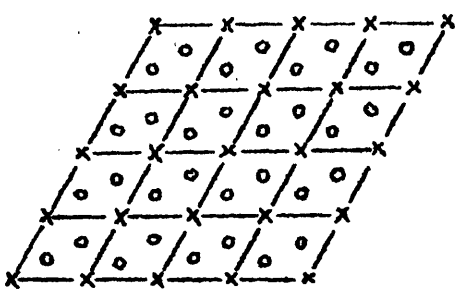
In the following discussion (a) will be represented by X and (b) by O.

It is not possible to represent other than the zero layer of the reciprocal structure without introducing phase

shifts at the diffracting holes. (Three dimensional transforms have been produced by using circularly polarised light and introducing phase shifts with mica half-wave plates; Harburn & Taylor (1961).)

(a) First attempts involved the introduction of disorder into otherwise ordered arrangements. It was found that a block of 16 R cells with molecules all oriented similarly was sufficient to give adequately sharp spots in the optical transform. 16 R cells are of course equivalent to 48 primitive units. The transform is shown in figure 16 .

(b) 16 cells, arranged as would be required for P3C1 below, although the number of repeats is smaller, gave only



sharp spots with, of course, the extra spots corresponding to $-h+k+l \neq 3n$. (figure 16a).

(c) Keeping the molecules defining the cell corners for P3C1 regularly oriented but arranging the internal molecules randomly gave diffuse scattering which was however continuous rather than discrete. Both (b) and (c) would lead to an

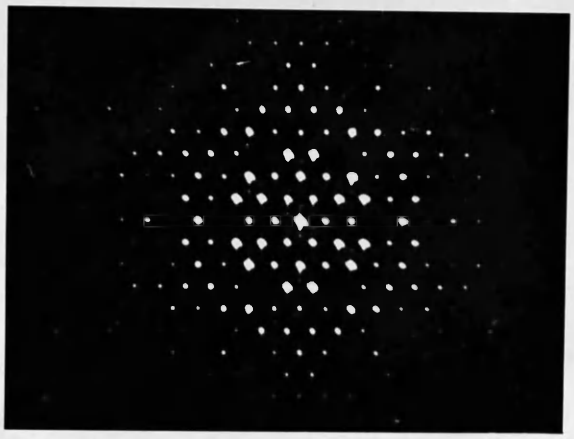


Figure 16.

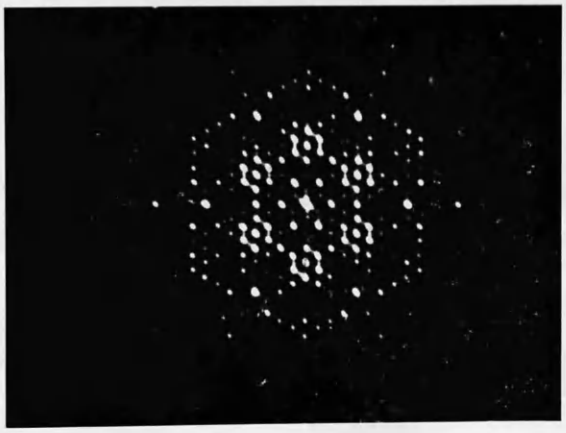


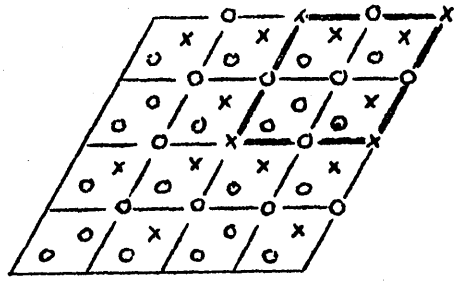
Figure 16a.

averaged structure with occupancy ratios 0.67:0.33.

(c) Corresponds to a random structure superimposed on a regular one rather than local ordering.

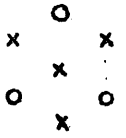
(d) A next approach was to make the repeat unit larger but to keep the same total number of molecules in the mask.

This was attained by interchanging a pair of X and O molecules at the corners of a cell as below.



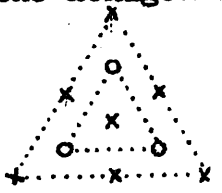
This model gave diffuse hexagons but the transform did not possess hexagons oriented as in the x-ray photographs (figure 17). One characteristic of the model is however that there are now only limited linear concentrations of similarly oriented molecules and this gave the idea that a model based on linear concentrations rather than on cells of various sizes should be tried.

(e) The model above , although possessing too few molecules to give discrete sharp spots, and also being too weak to see properly in the microscope, appeared promising. It was felt that the model should possess an overall three-fold axis and initially ideas were tried with various hexagons of molecules around one.



The model above was not unpromising but extensions of this to further hexagons tended to quickly give discrete rather than diffuse patterns. Hexagonal concentrations rapidly gave 1:1 ratios.

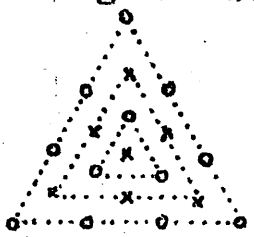
(f) Reverting again to linear concentrations based on the triangle rather than the hexagon suggested the model below



The optical transform of this model is shown in figure 18(c) and can be seen to be in very fair agreement with the X-ray photograph.

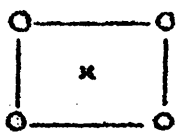
Any additions to this tending to produce a hexagonal array had the effect of producing discreteness again but the addition of a further triangle again gave a transform very

like the photographs; figure 18b).



The ratio of X to 0 is 0.37 : 0.63; quite close to the observed ratio 0.39 : 0.61.

If this triangular packing were to continue indefinitely the occupancy ratio would tend to 1:1 and ultimately would be equivalent to three twinned crystals at 120° to each other, each having the arrangement,



and would eventually produce discrete spots at the centres of the faces of the diffuse hexagons.

At this point it was realised that two different scattering units at the X and 0 sites could just as well possess the diffuse streaking in their transforms, although not of course the observed intensity variation. This was checked by representing the X-molecules as open holes at their centres and the 0-molecules by holes covered with one thickness of cellotape. Perhaps a more obvious method would have been to have used holes of different sizes but, owing

to past misuse, the pantograph punch had one size of punch jammed in which proved impossible to remove without major dismantling. The open and covered hole model has one compensating advantage in that the cellotape is readily removed to produce a different arrangement. The transform of a model corresponding to the larger triangle model is given as figure 19) The actual transform produced by projections of molecules can be regarded as a convolution of this transform with the transform of an oriented single molecule of TMSM.

(g) The production of linear arrays of diffuse spots on hexagons with the development of order was illustrated with the hole and cellotape masks. In this case it was decided to approach P3c1. A six by six array of cells oriented as for R3c was punched out on half the previous scale. In all there were 121 holes. 121 random numbers were generated by a method similar to that used in a digital computer i.e. by squaring a number and then selecting part of the product and squaring this. Six figure numbers were used and, if the number formed by a fixed internal triad was divisible by three, the appropriate hole was covered with cellotape to approximate to a 2:1 ratio. A photograph of the original transform is shown in figure 20). A set of three pairs of molecules related as nearly as possible by a three fold axis were then

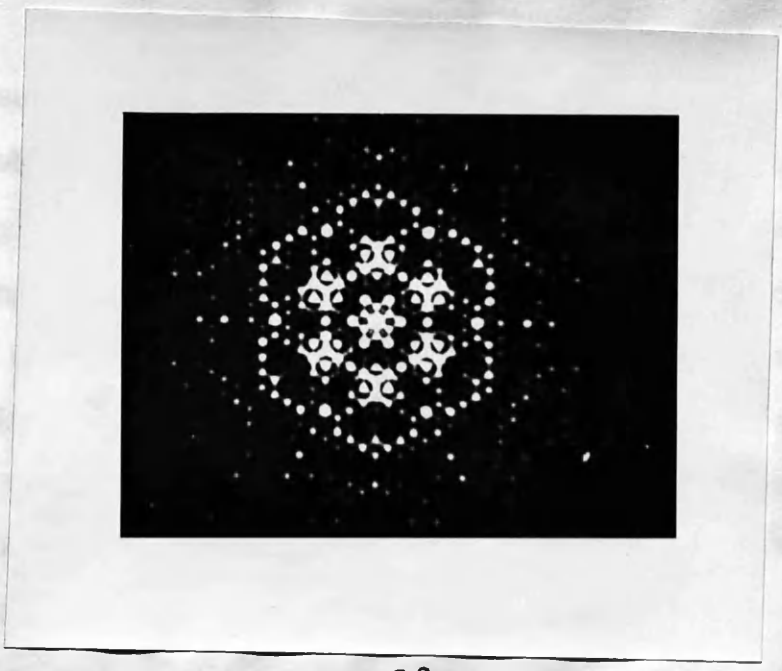


Figure 18a.

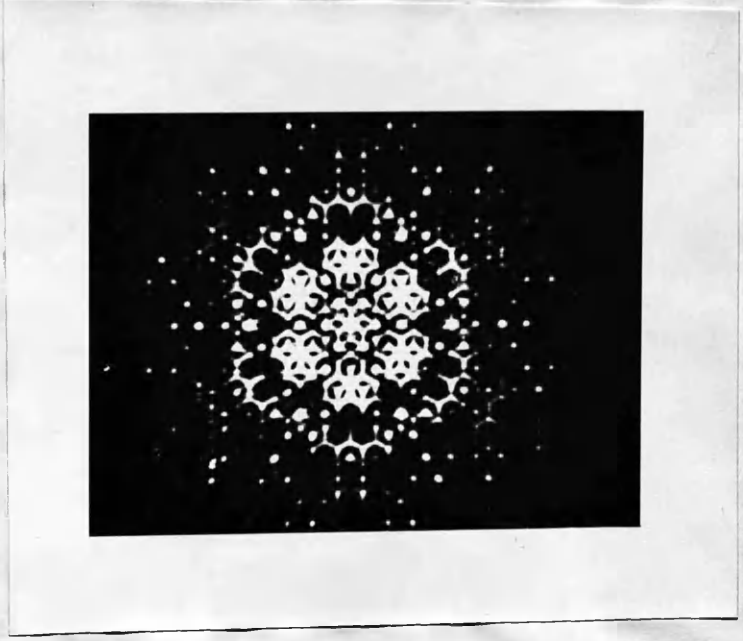


Figure 18b.

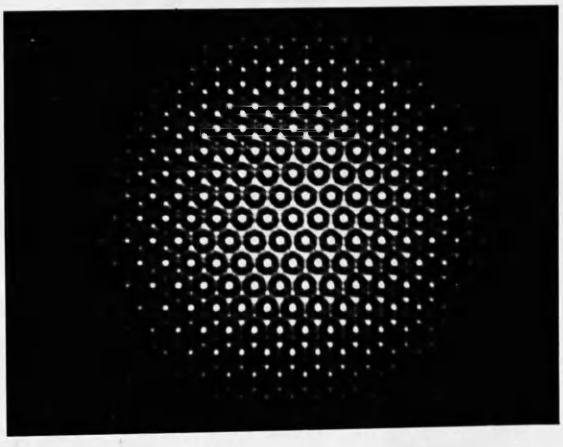


Figure 19.

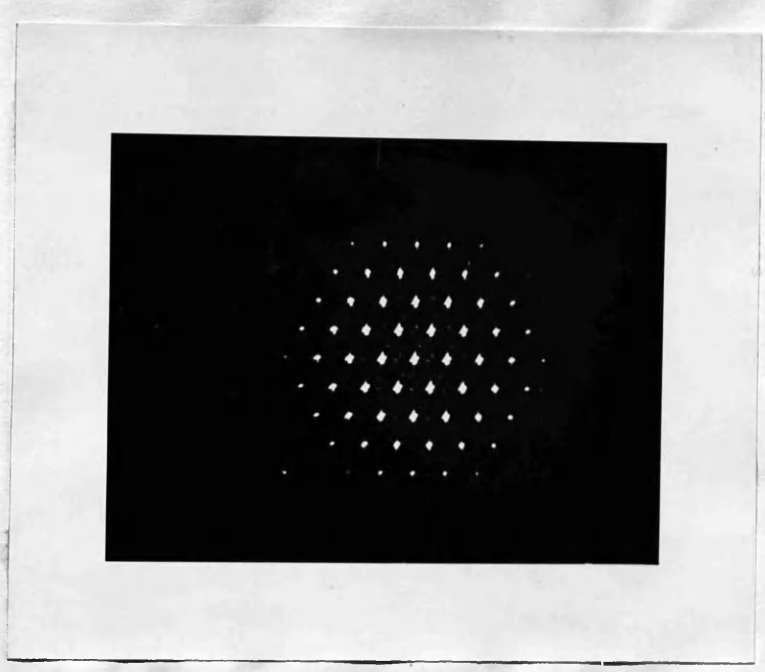


Figure 20.

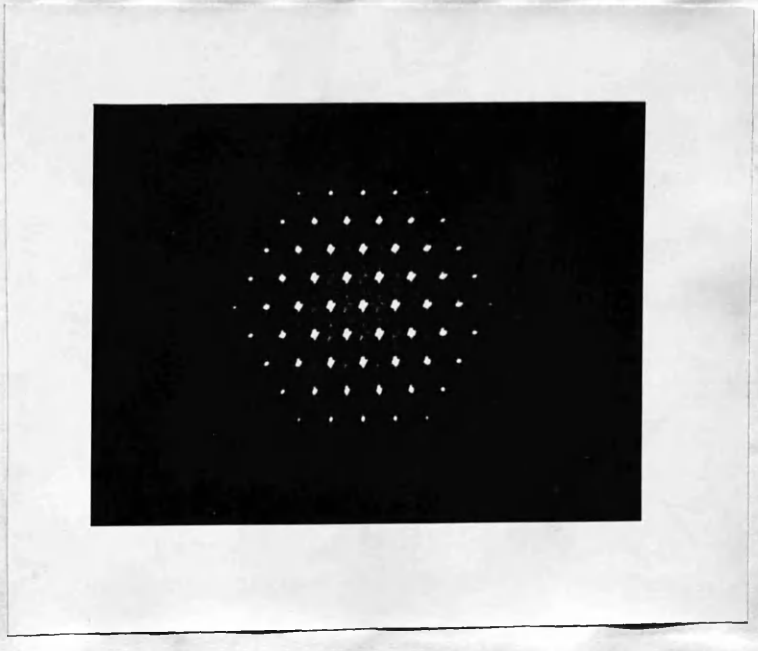


Figure 21.

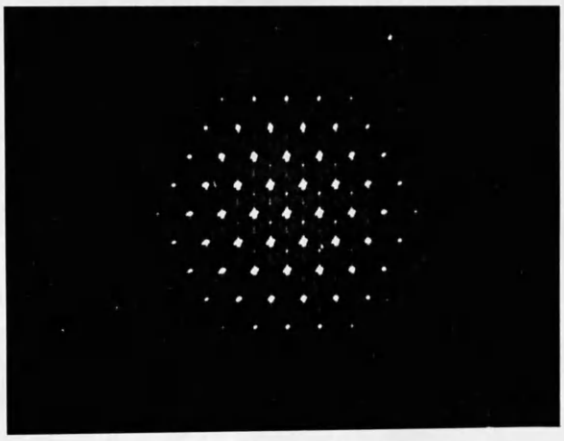


Figure 22.

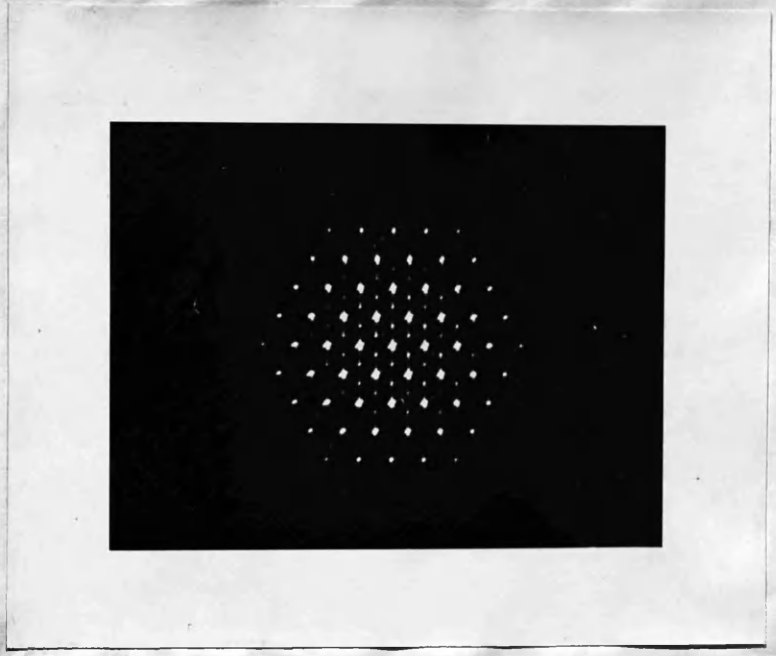


Figure 23.

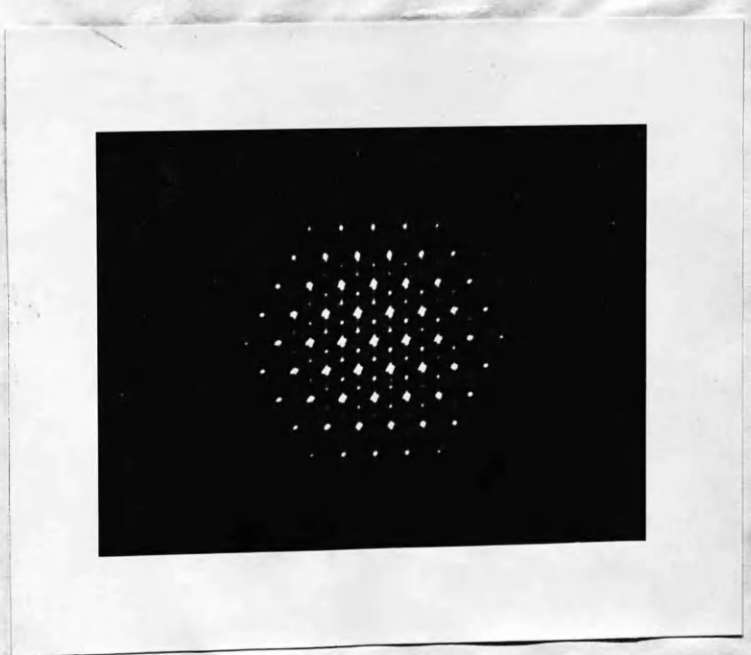


Figure 24.

interchanged to give positions required by P3c1. The gradually development of linearity is shown in photographs (21) and (22) with respectively 3 and 6 pairs interchanged, with 9 and 12 pairs as in figures 23) and 24) the diffuse scattering decreases and the P3c1 pattern is developed, although figure 24) is due to a transform possessing 23 molecules in places not required by a regular arrangement. The first transform is of a model with 47 molecules wrongly placed for space group P3c1.

At this point it is relevant to consider the observations on a basis of the packing of molecular stacks with the coordinates given by the last cycle of refinement.

PACKING OF STACKS OF MOLECULES

There are two arrangements which require consideration for molecular distances; other arrangements do not give any different distances.

(a) The first situation is that shown in figure 25 , i.e. a completely ordered arrangement in R3c. There are some fairly short distances but none are unreasonable although it is true that some oxygen atoms in different stacks are fairly close and, quite possibly, there will be a tendency for these polar atoms to turn away from each other. Not all distances are indicated but all independent ones below 4 Å are shown.

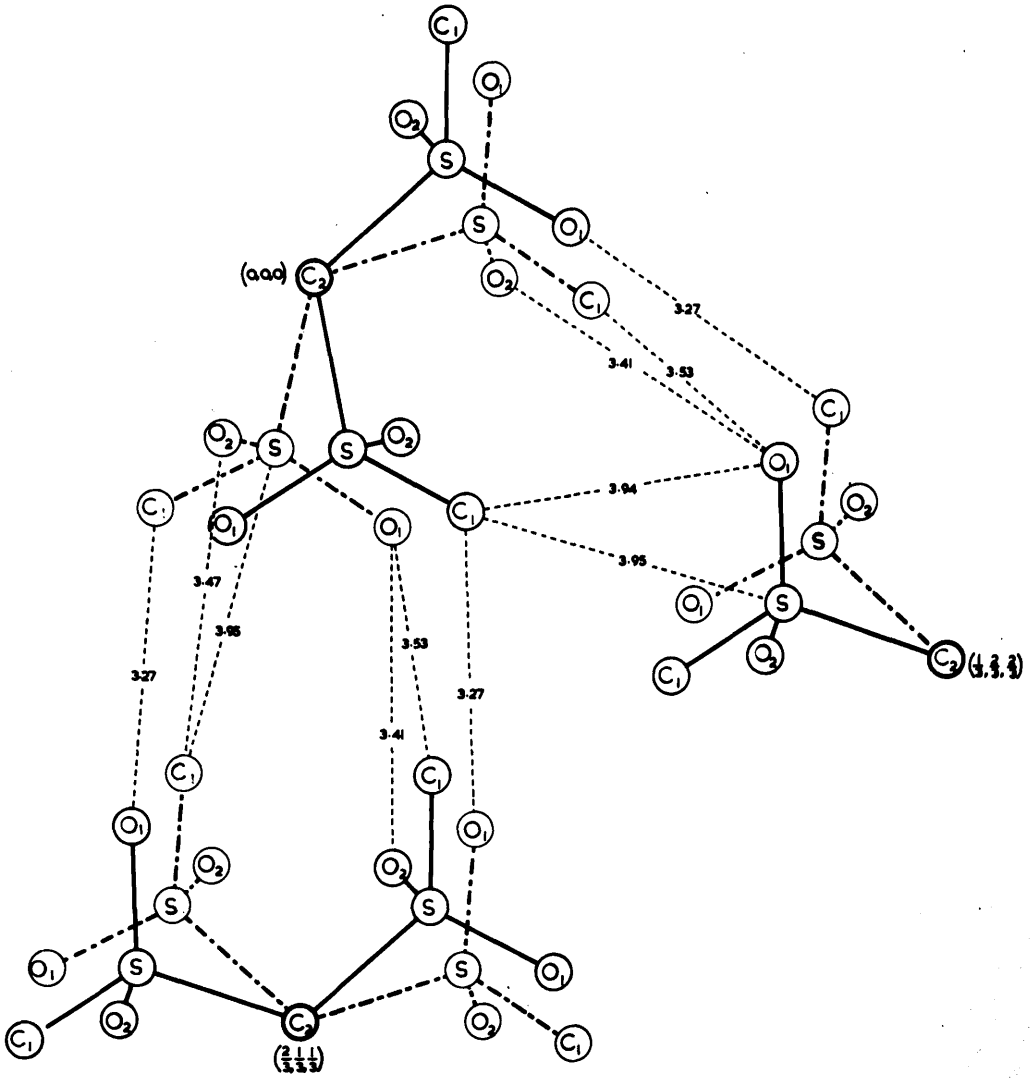
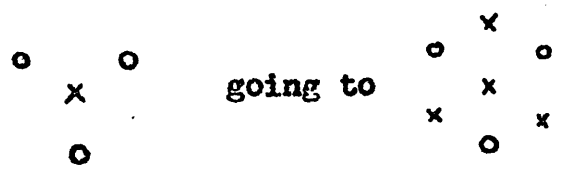


Figure 25.

(b) The second situation, that of a molecular stack with one orientation completely surrounded by a hexagon of stacks of different orientations is shown in figure 26). The situation here is radically different. The pair of stacks arranged vertically above each other in the diagram possess no close O-O contacts but the other differently arranged pair, although the distances are not impossibly short, have a pair (symmetrically related) of O-O contacts which are quite short, being 3.25 Å. Thus it seems likely that a given molecule would tend to have a triangle of oppositely arranged molecules but not a hexagon.

However, if a molecular stack is allowed to have a triangle of differently arranged molecules, it becomes impossible to fit in other stacks without producing short contacts.



respect to the central molecule but not with respect to the O molecules which now have short contacts with the added X molecules.

The situation in an ordered crystal arranged for P_3Cl is shown overleaf.

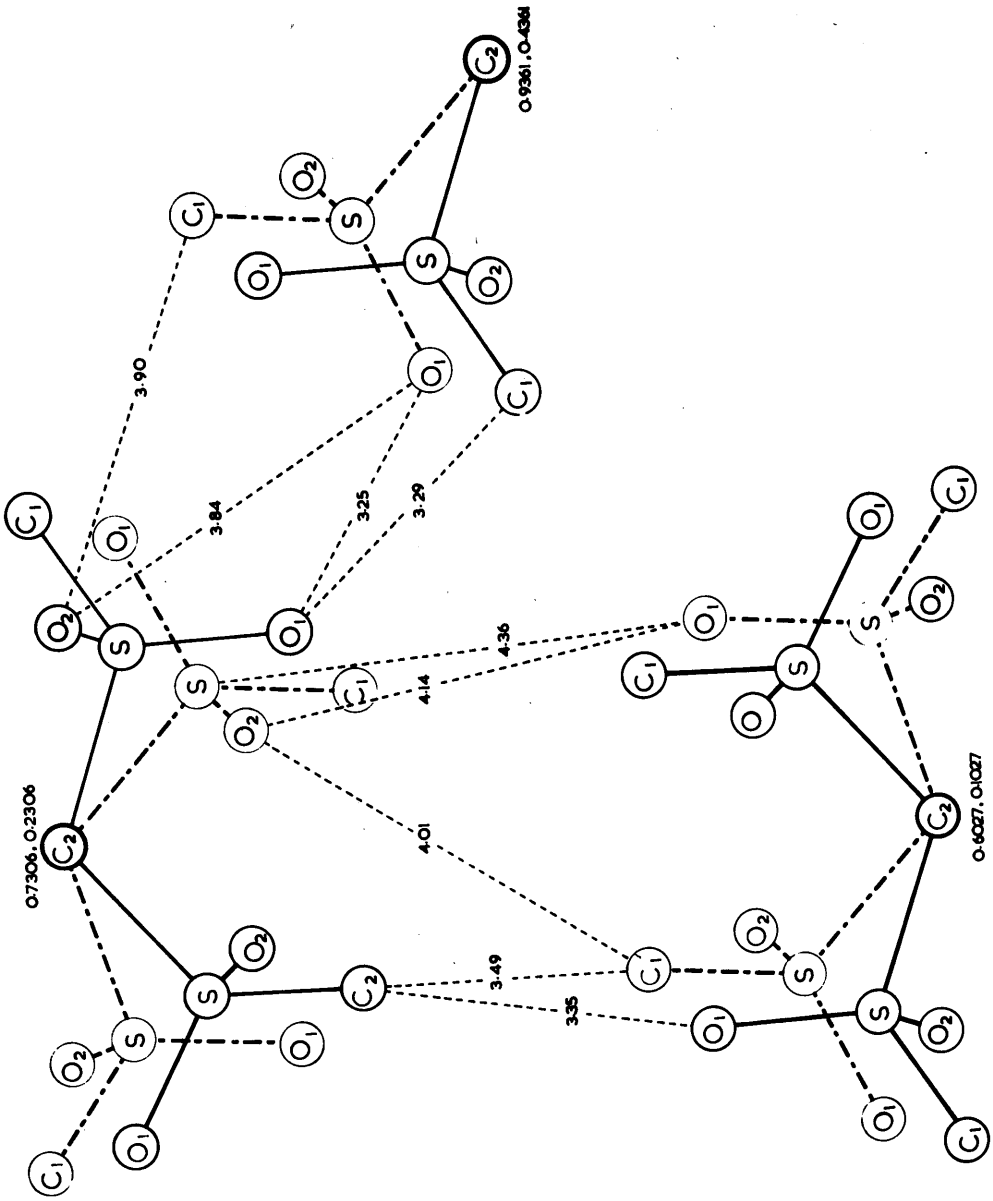
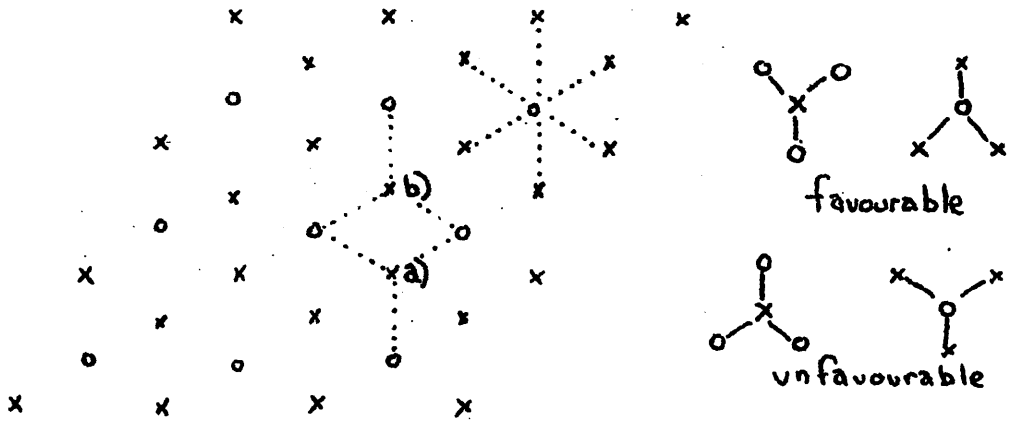
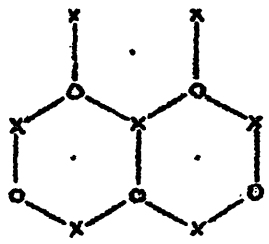

0.9361, 0.4361
0.7306, 0.2306
0.6027, 0.1027
3.90
3.84
3.25
3.29
4.36
4.14
4.01
3.49
3.35

Figure 26.



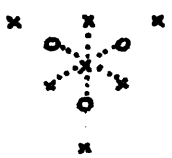
The situation allows molecule (a) to have a favourable environment but requires molecule (b) to have an unfavourable one. Also the O molecules have three molecules favourably oriented but three unfavourably. The best compromise to an unprejudiced observer might be for the whole unit cell to be ordered R3c but the process of crystal growth may allow one molecule to attain its favourable environment and then any method of fitting the next few molecules produces an unfavourable situation. The actual disorder must be a compromise between two competing processes, one tending to complete order and the other to a favourable local orientation.

If only 2/3 of the sites were occupied the molecules could be arranged favourably in hexagons as below:—

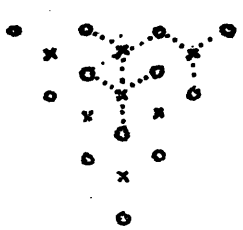


However the central molecule is placed, and the observed density of the crystals does not indicate that there are many gaps, the situation is unfavourable with respect to an X or O molecule. One point which makes this hexagonal arrangement unlikely is the observed occupancy ratio 0.61 : 0.39 which would require the central molecules to be 5/6 of one sort to 1/6 of the other and this ratio is too small to explain the observed diffuseness. This can be seen if the approach from randomness to order is considered; where there were 23 randomly misplaced molecules in 121 the diffuse spots had become extremely weak.

If one next considers the triangle models which reproduced the diffuse streaking well one can see that there is, in the two cases considered, a combination of arrangements which are both favourable and unfavourable.



In the smaller arrangement above the central molecule has a favourable environment but the triangle of O orientations has an unfavourable arrangement apart from the central X.



In the larger arrangement the X molecules now have as near a favourable environment as possible, given the central arrangement and the centre triangle of O molecules.

The triangle arrangement is probably not a complete explanation. It would be possible for the crystal to be built up of small units like these triangles, arranged, relative to each other, randomly. Small integral translations of triangles with respect to one another would leave only small areas to be filled in some other fashion which would not affect the overall ratio of orientations greatly but perhaps the model may best be regarded as an analogue of the situation in the crystal.

The major difficulty in attaining a more exact idea of the nature of the disorder is in the lack of knowledge of how the crystals actually grow. Their direction of maximum growth is parallel to the c axis which is consistent with dipole-dipole attraction in this sense but the actual pattern of growth would seem to be probably decided by the initial deposition on the 001 plane. The fact that the occupancy ratio is not 1:1 may suggest that there is a greater tendency for the molecules to be oriented in one particular direction on the surface on which growth commences.

Given that one initial orientation is favoured, one can suggest a method of producing limited lines of differently

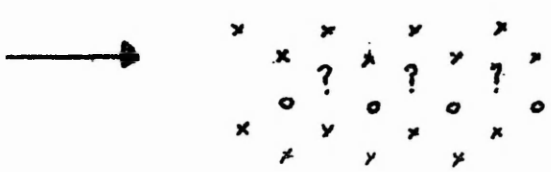
oriented molecules which gives approximately the correct ratio.

If one considers a growth front composed of similarly oriented molecules, a apart and allows, perhaps, the molecule at the end of the row to attain the favourable triad of oppositely arranged molecules, there might then be a tendency for the other molecules in the row to also attain this situation as far as possible.

The o molecules could also attain their favourable environment by adding a line of x's.

If the row at the centre of the partial hexagons is now to be filled, one could suggest perhaps an even chance of the orientation being X or O.

The row of X's above this random row might then add another row of X's, if the chances of the ordered and most favourable orientations are about even, giving the following situation and the chances would then be



that the next row would be a row of O's.

This fairly naive argument would lead to a ratio of X to O of $2\frac{1}{2}$: $1\frac{1}{2}$ i.e. 0.625 : 0.375.

POSSIBLE FURTHER APPROACHES

It is possible that the substrate on which the crystals form causes the observed prevalence of one orientation. Attempts have been made to grow crystals by sublimation in an effort to find out whether such crystals have a different degree of disorder. However, so far, although the sublimate has been crystalline, the crystals are much too small to consider investigating by X-ray methods.

It is also possible that electron microscopy might give some indication as to whether the idea of linear concentrations is correct but there are difficulties in the way of preparing suitable specimens for this method.

TABLE 1.

OBSERVED AND CALCULATED STRUCTURE FACTORS

The scale on which these structure factors are calculated is 1.64 times that required for one primitive unit. It was convenient to vary only the scattering factors for the atoms with the lower occupancy factors and to keep the others constant. (1:0.64 = 0.61:0.39)

h	k	l	|F|	|F|	α°
0	0	6	78	86	353
		12	14	15	344
0	1	2	75	73	202
		8	34	38	194
0	2	4	31	35	177
		10	15	15	177
0	3	6	10	12	118
0	4	2	31	37	359
		8	36	34	356
0	5	4	11	13	216
		10	15	13	191
0	6	6	7	7	3
0	7	2	31	34	356
		8	7	8	191
0	8	4	17	19	353
		10	8	7	355
0	9	6	13	14	183
0	10	8	10	13	6
0	11	4	15	16	194
0	14	4	18	20	356
1	0	4	26	27	30
		10	3	6	106
1	1	0	88	90	0
		3	5	6	85
		6	25	26	350
		12	11	10	356
1	2	2	49	50	359
		5	11	9	340
		8	16	18	1
1	3	1	31	32	8
		4	33	37	191
		7	20	20	7
		10	14	15	193
		13	6	5	3
1	4	3	5	6	0
		6	21	20	154
		9	7	4	340
1	5	2	13	15	347
		5	7	6	181
		8	16	15	352
1	6	7	10	8	145
		10	6	5	190
1	7	3	22	23	9
		6	11	10	327
		9	14	13	0
1	8	2	13	11	168
1	9	1	15	16	186
		4	15	18	352
		7	8	8	188
1	10	3	8	8	141
		6	12	12	165
1	11	2	18	20	357
		5	10	17	3
		8	9	11	357
		11	10	9	0
1	12	4	9	10	184
1	15	4	15	16	357
2	0	2	33	35	182
		8	8	7	172
2	1	1	28	28	12
		4	28	27	0
		7	12	15	19
2	2	0	83	83	180
		3	20	17	15
		6	34	31	176
		9	11	7	315

h	k	l	|F|	|F|	α°
2	3	2	7	8	24
		5	11	10	131
		8	23	22	8
		11	4	7	173
2	4	1	32	29	15
		7	19	20	2
		10	10	10	188
2	5	3	19	20	358
		9	14	14	354
2	6	2	19	18	188
		5	19	17	216
		11	6	8	198
2	7	1	45	43	173
		4	23	24	10
		7	21	23	167
		10	10	9	4
2	8	3	27	27	14
		6	9	11	198
		9	16	15	13
2	9	5	26	25	358
		11	10	10	347
2	10	4	12	11	180
2	11	3	21	19	170
3	0	0	59	59	199
		6	52	45	188
		12	11	10	186
3	1	2	67	59	163
		8	7	9	77
3	2	1	42	45	22
		4	16	18	1
		7	41	40	2
		10	10	11	349
3	3	0	24	26	180
		3	17	17	330
		6	10	8	181
3	4	2	22	21	187
		5	17	15	173
		11	7	8	182
3	5	1	29	28	170
		4	13	13	29
		7	17	19	164
3	6	3	39	38	2
		9	21	22	359
3	7	2	34	31	179
		8	14	11	165
3	8	1	21	24	179
		4	8	7	17
		7	12	11	185
3	9	3	13	10	148
3	10	5	24	27	3
		11	11	10	2
4	0	4	76	83	359
		10	29	33	357
4	1	0	11	13	280
		3	14	11	327
		6	29	28	192
		12	13	16	187
4	2	2	21	20	174
		5	14	13	132
		8	7	9	159
4	3	1	22	17	3
		4	16	18	164
		7	13	15	350
4	4	0	31	27	0
		6	15	17	3

h	k	l	|F|	|F|	α°
4	5	2	50	47	182
		5	12	13	206
		8	13	14	186
		11	8	7	186
4	6	1	29	25	171
		4	11	10	21
		7	16	15	168
4	7	3	15	14	352
4	9	1	9	5	335
4	10	3	8	11	174
5	0	2	67	68	173
		8	20	18	164
5	1	1	29	29	7
		4	34	35	2
		7	15	18	355
		10	13	14	359
5	2	0	21	19	3
		3	32	33	182
		6	19	17	353
		9	18	20	180
5	3	2	9	8	232
		5	15	18	4
		11	11	11	5
5	4	1	19	16	223
		4	19	17	165
		7	15	14	191
		10	0	17	5
5	5	0	17	15	0
5	6	2	8	9	124
		5	15	19	176
5	7	1	27	26	6
		7	18	17	4
6	0	0	39	36	353
		6	8	10	217
		12	7	6	194
6	1	2	14	15	346
		5	19	18	7
		11	11	12	8
6	2	1	24	22	382
		4	19	19	174
		10	12	12	178
6	3	0	33	29	12
		3	40	43	171
		6	22	21	7
		9	21	20	168
6	4	2	13	11	200
		11	6	7	2
6	5	1	22	22	356
		7	12	10	355
6	6	0	22	22	180
		3	13	15	213
		6	17	16	180
		9	12	11	201
6	7	2	15	17	11
		5	21	22	170
6	8	1	18	17	4
		4	14	12	349
		7	20	17	2
6	10	2	10	10	184
7	0	4	23	21	351
		10	14	14	188
7	1	0	21	20	9
		3	32	33	172
		9	12	12	171
7	2	2	14	16	341
		5	42	40	2
		11	17	18	0

h	k	l	|F|	|F|	α°
7	3	1	15	15	219
		4	17	17	173
		7	11	12	209
7	4	0	8	9	159
		3	10	9	181
		6	9	9	173
7	5	2	12	11	9
		5	17	14	167
7	6	1	35	37	6
		4	12	13	342
		7	19	22	5
7	7	0	11	11	187
7	9	4	8	9	5
8	0	2	23	26	357
		8	23	19	352
8	1	1	7	6	216
		4	7	5	236
		7	11	10	198
		10	11	11	190
8	2	0	4	5	38
		3	10	9	149
8	3	5	15	15	1
		11	7	5	346
8	5	0	9	8	175
		6	10	12	178
9	0	6	11	12	163
9	1	2	8	5	26
		5	16	18	0
9	2	1	21	24	173
9	3	0	6	6	199
		3	22	24	11
		9	12	12	4
9	6	0	8	8	5
9	9	0	7	7	180
10	0	4	11	11	344
		10	6	5	349
10	1	0	17	16	188
		3	11	11	16
		6	14	13	186
		9	9	8	6
10	2	2	13	15	170
10	3	1	18	20	172
10	4	0	16	16	358
		3	12	16	6
11	0	2	16	13	165
11	2	0	9	7	327
		3	17	19	11
		9	9	12	2
11	3	2	16	19	185
11	5	0	11	13	7
12	0	0	5	7	208
		6	15	14	195
12	1	2	13	11	175
12	3	0	19	17	359
12	6	0	6	5	6
13	0	4	10	10	354
13	1	0	9	7	5
13	4	0	5	5	352
14	0	2	14	17	358
14	1	4	10	8	202
15	0	0	8	8	143
15	1	2	19	19	358
15	3	0	6	6	189
16	1	0	6	6	160
18	0	0	8	8	3
19	1	0	9	8	0

UNOBSERVED STRUCTURE FACTORS

The observed values tabulated were obtained by applying the appropriate polarization and kinetic factors to the minimum intensity on the step wedge. The amplitudes are then to be regarded as less than the given value.

The average calculated value is 0.56 times the average 'observed' value and only four reflexions have calculated values greater than the minimum observable.

h	k	l	|F$_o$|	|F$_c$|	α°
0	9	0	6	3	299
0	10	2	8	6	53
0	13	2	10	6	0
1	1	9	4	3	316
1	2	11	3	1	126
1	5	11	5	4	194
1	6	4	6	5	352
1	8	5	9	5	287
		8	14	6	168
		11	6	3	291
1	9	7	12	8	188
		10	7	4	342
2	1	10	4	3	328
2	4	4	7	2	177
2	5	6	7	2	261
2	6	8	13	10	178
2	9	2	8	5	173
2	10	1	10	4	258
2	12	2	10	5	217

h	k	l	|F$_o$|	|F$_c$|	α°
3	1	5	6	3	136
		8	8	9	77
		11	4	4	151
3	3	9	6	3	280
3	4	8	13	0	2
3	5	10	6	2	95
3	6	5	8	6	312
3	9	6	10	5	169
3	10	2	9	4	228
4	1	9	5	5	226
4	2	11	5	3	110
4	3	10	5	3	147
4	4	3	6	2	102
		9	7	1	144
4	6	10	7	8	9
4	7	6	9	4	208
4	8	2	9	4	26
		5	10	5	13
4	9	4	9	2	191

h	k	l	|F$_o$|	|F$_c$|	α°
5	3	8	12	10	200
5	4	10	6	4	127
5	5	3	7	7	200
		6	9	4	23
		9	8	4	176
5	6	11	7	6	167
5	7	4	8	4	312
5	8	3	8	5	211
		6	10	7	178
5	9	2	9	6	179
		5	11	3	161
		7	12	7	232
6	2	5	9	10	7
6	4	5	8	2	338
6	5	4	7	6	156
6	7	11	8	0	201
7	1	6	7	4	155
7	5	11	7	1	180
7	7	0	10	2	8
7	8	2	9	2	66
8	2	6	8	4	86
		9			

h	k	l	|F$_o$|	|F$_c$|	α°
8	3	2	7	7	308
8	4	1	9	5	149
		4	8	6	353
		7	13	3	15
8	5	3	8	4	303
8	6	2	9	8	7
		5	11	10	166
8	7	4	10	8	342
8	8	0	9	2	180
9	3	6	10	4	191
9	4	2	9	9	172
		5	10	6	206
9	5	1	9	2	64
10	2	5	10	8	328
10	3	4	9	5	24
10	5	2	10	8	202
12	2	4	10	4	31

PART III

INVESTIGATIONS IN NATURAL PRODUCT STRUCTURE

(a) PYRETHROSIN AND TENULIN.

(b) THE CRYSTAL AND MOLECULAR STRUCTURE OF CALYCANTHINE DIHYDROBROMIDE.

(a) PYRETHROSIN AND TENULIN

The study of these two compounds was undertaken as part of a general programme of research into the structures of sesquiterpenoid compounds. The two compounds are isomeric and have formula $C_{17}H_{22}O_5$. At the time that the work was carried out little was known of the details of the structures, although the structure of pyrethrosin has been worked out since then by Barton, de Mayo and Bockman (1957, 1960) by chemical methods. Both compounds proved to have complex structures and attempts to prepare heavy atom derivatives were absortive. Hence this study was not carried beyond the determination of unit cell symmetry and dimensions.

(i) Pyrethrosin

Pyramidal crystals from ethanol, c axis corresponds to axis of pyramid.

Tetragonal, absent spectra h00 for $h \neq 2n$

00l " $l \neq 4n$

Space group $P4_12_12$ (D_4^4) or $P4_32_12$ (D_4^8) - enantiomorphic

Dimensions, from precession photographs Cu Kα X-radiation used because of length of c axis

$a = b = 8.07 \pm 0.01$ Å, $C = 49.72 \pm 0.04$ Å, $V = 3,253$ Å^3, $Z = 8$

Density (by flotation) = 1.27 g/cc

Density (from X-ray measurements, assuming $Z = 8$) = 1.27 g/cc.

The space group has 8 general positions and hence no information can be deduced about molecular symmetry.

(ii) Tenulin

Small flat plates crystallised from benzene were provided by Dr. de Mayo. These crystals are a benzene adduct and are unstable, probably due to the release of solvent of crystallization. Crystals from ethanol and ethanol/benzene were very small. Although tenulin is labile in weakly alkaline solution and in fact could not be crystallized from water in London, it was possible to obtain good crystals by very slow crystallization from Glasgow tap water.

Crystals ; flat prisms.

Orthorhombic, absent spectra,

h00 for h odd, 0k0 for k odd, 00l for l odd.

Space group; $P2_1\,2_1\,2$ (D_2^3)

Cell dimensions (precession photographs, CuKα X-radiation)

$a = 28.47 \pm 0.03$ Å, $b = 10.56 \pm 0.02$ Å, $c = 10.54 \pm 0.02$ Å

$V = 3169$ Å^3 $Z = 8$

Density (by flotation) = 1.30 g./cc

Density (from X-ray measurements, assuming Z = 8) = 1.29 g./cc

The dimensions are approximately tetragonal, and, although the b and c axes have lengths resembling somewhat the length of the 110 diagonal of pyrethrosin (11.4 Å), there is no doubt that the crystal symmetry is orthorhombic.

The asymmetric unit contains two molecules of tenulin and thus no information about structure can be deduced.

b) THE CRYSTAL AND MOLECULAR STRUCTURE OF CALYCANTHINE DIHYDROBROMIDE.

INTRODUCTION

There has been considerable interest in calycanthine since its first isolation by Eccles in 1888 from the seeds of the shrub Calycanthus Glaucus (Willd.), native to Georgia, North Carolina and Tennessee. The impetus for the isolation seems to have been that rabbits fed with the seeds died in convulsions.

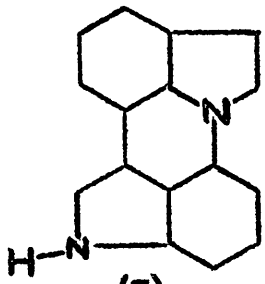
In 1905 Gordin assigned the formula $C_{11} H_{14} N_2$ and also described its crystalline form as orthorhombic bipyramidal. He described various salts, notably a hydrobromide and hydrochloride and also a chloroplatinate and chloroaurate. The hydrohalides were assigned the formula $C_{11} H_{14} N_2 X. H_2O$.

In 1925 Spath & Stroh doubled the molecular formula giving $C_{22} H_{28} N_4$.

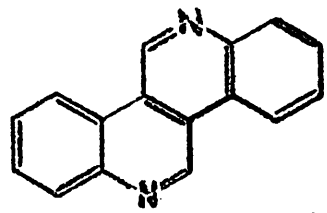
Somewhat later, in 1939, the formula was revised to the correct one $C_{22} H_{26} N_4$ by Barger, Madinaveitia & Streuli.

In between these dates, in 1929, Manske had isolated calycanthine from the seeds of a Composite, Meratia praecox. The occurrence of the same alkaloid in two unrelated plants suggested that there might be a simple biological route for its preparation. This was in accordance with the fact that pyrolysis of calycanthine yielded N-methyl tryptamine.

Barger et al. also described the isolation of a degradation product, the weak base calycanine, to which they assigned structure (I).

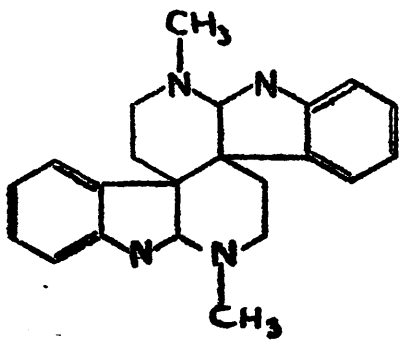


(I)

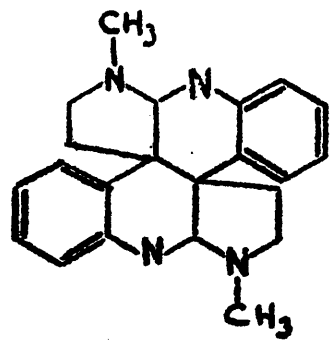


(II)

In 1954, Robinson and Teuber determined the correct structure of calycanine (II) and suggested various formulae for calycanthine, favouring (III), but noting that other possibilities existed, notably (IV). This was the position when the X-ray work on the structure was started.



(III)



(IV)

PRELIMINARY CRYSTAL STRUCTURAL WORK

In 1957, crystals of pure calycanthine and its hydrochloride and hydrobromide were supplied by Dr. Harley-Mason. These salts are dihydrates and are liable to lose water of crystallisation in a dry atmosphere. It was found however that they were quite stable in a deep-freeze unit and, in the high atmospheric humidity of Glasgow, they are sufficiently stable to allow collection of X-ray data.

It was hoped that examination of several derivatives using isomorphous replacement or heavy-atom methods would allow recognition of the molecular units with two-dimensional techniques. Accordingly preliminary investigations were carried out on the pure substance and several salts. Because the hydrohalides supplied by Dr. Harley-Mason had been dehydrated, crystals of these were prepared from the pure substance and crystallised from ethanol/water.

The hydrobromide and hydrochloride were readily prepared as dihydrates. The hydroiodide, although Gordin prepared it and stated that it was probably not hydrated, proved extremely difficult to make. Only one crystal was ever obtained and this decomposed during preliminary investigation. Hence unit cell details can only be reported approximately.

The crystalline form of calycanthine is orthorhombic bipyramidal and, although the substance was pure, the crystals were pinkish-brown in colour. The hydrochloride and hydrobromide were orthorhombic prismatic in form and colourless, while the hydroiodide crystal was rather more platy in appearance and distinctly yellow.

The hexachloroplatinate was also readily prepared; bright red needles separated slowly from aqueous solution. It was interesting to note that, although they appeared dendritic, the crystals were actually single.

The preliminary information is summarised in the following table.

	Space-group	a	b	c (Å)
Calycanthine.	$P2_12_12_1$ (D_2^4)	10·5	13·3	14·5
Calycanthine dihydrochloride dihydrate.	$P2_12_12_1$ (D_2^4)	9·5	13·9	17·0
Calycanthine dihydrobromide dihydrate.	$P2_12_12_1$ (D_2^4)	9·6	14·1	17·0
Calycanthine dihydroiodide.	Monoclinic?, $\beta=120°$,	9·5	13·8	8·9
Calycanthine hexachloroplatinate.	$P4_{1,3}22$ $(D_4^{4,8})$	13·4	13·4	31·9

It will be seem that, while calycanthine crystallises in the same space group as its hydrochloride and hydrobromide, it is not isomorphous with them. The hydroiodide might perhaps have been the most suitable for structural investigation but the difficulty of preparation and the

instability of the crystals precluded this. The structure of the hexachloroplatinate appears to be somewhat complex.

It was obvious that the crystals whose structures stood the best chance of solution were those of the isomorphous hydrobromide and hydrochloride especially as the axial projections of space-group $P2_1\ 2_1\ 2_1$ are centrosymmetric. In actual fact most of the work was done on the hydrobromide, although the isomorphous replacement method was used on the 100 projection. However this did not add any information to that given by the standard heavy-atom technique.

SPACE GROUP AND CELL DIMENSIONS

Calycanthine dihydrobromide dihydrate, $C_{22}H_{28}N_4Br_2 \cdot 2H_2O$

Orthorhombic, absent spectra hOO for h odd,
OkO for k odd,
OOl for l odd.

Space-group $P2_12_12_1$ (D_2^4)

Cell dimensions (Precession camera; Mo $K\alpha$ X-radiation, $\lambda = 0.7107$ Å; photographic measurements corrected for film shrinkage.)

$a = 9.61 \pm 0.01$, $b = 14.13 \pm 0.02$, $c = 16.97 \pm 0.02$ Å

$V = 2304$ Å^3, $Z = 4$

Density (calculated for four molecules in the unit cell) = 1.568 g/cc.

Density (measured by flotation in CCl_4/benzene) = 1.568 g/cc.

The exact agreement in density is probably fortuitous as the probable error in the measured density is at least 0.005 g/cc.

STANDARD PROJECTIONAL WORK ON THE STRUCTURE

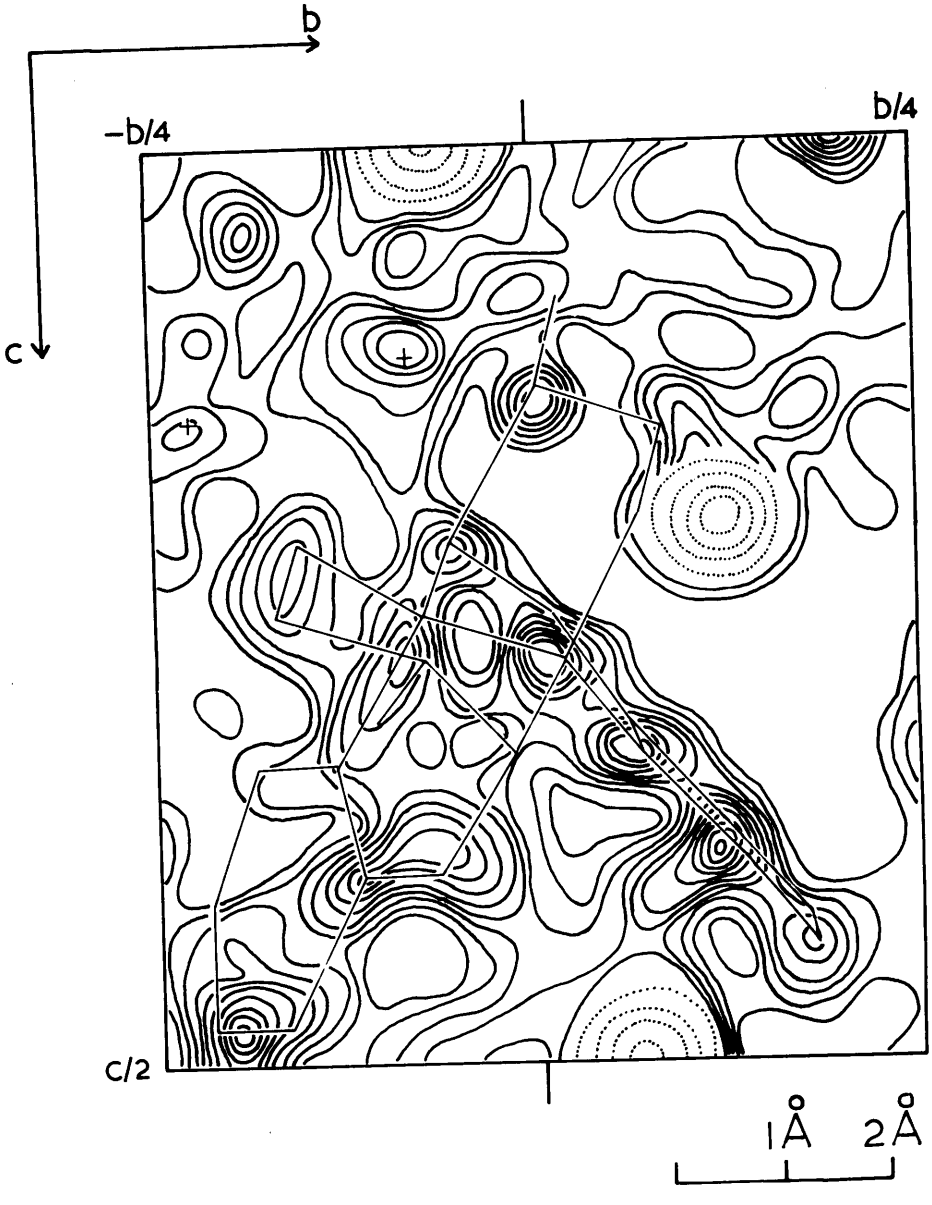
In this work the various fourier series were calculated using Beevers-Lipson strips and also the Robertson fourier machine RUFUS (mentioned in the introduction). The choice of method was decided by the availability of RUFUS.

Okℓ data was collected for the hydrobromide by Weissenberg photographic methods using Cu Kα X-radiation and the multiple film technique (Robertson (1943)).

The intensities were estimated by comparison with a step-wedge made with the actual crystal used for recording the data.

A Patterson projection on 100, was calculated using RUFUS, and it was possible to determine the bromine y, z coordinates uniquely by using not only peaks due to symmetry related atoms but also peaks between independent atoms. No structural information about the molecule could be deduced from the projection.

A similar collection of hoℓ data and calculation on RUFUS gave x,z coordinates with good agreement for the common z-coordinate. Coordinates were taken as the mean of the values obtained by using all the peaks in the Pattersons which could be assigned to Br - Br interactions.



100 Projection

Figure 24.

Using phases given by the bromines only, electron density projections were calculated on the 100 and 010 planes, in these cases with Beevers-Lipson strips (Lipson & Beevers, 1936).

It was not however possible to make any very definite deductions about the structure. Neither of the structures suggested could be recognised in the projections but it was not possible to suggest that either or both were wrong.

The projections were actually quite reliable. Figure 24) shows a comparison between the final structure and the 100 projection.

Fairly accurate bromine coordinates were obtained however from the projections as can be seen by comparison with the final, least-squares-adjusted, coordinates.

	Final coords.			Projection coords.		
	x	y	z	x	y	z
Br_0	-.1147	.4338	.5024	-.1167	.4311	.5040
Br_1	-.4787	.6204	.2936	-.4830	.6210	.2950

At this point, after reading Fridrichsons and Mathieson's (1955) very elegant paper on the determination of the structure of cryptopleurine, it was decided to try the method of generalised projections in the hope that more

information about the structure would be obtained by this partial three-dimensional method.

Before this was carried out, the isomorphous replacement method was used with 0kℓ data from both the hydrochloride and hydrobromide to calculate a 100 electron density projection but the density map was not significantly different from that given by the heavy-atom technique.

GENERALISED PROJECTION WORK ON CALYCANTHINE

The principles on which this part of the investigation are based are detailed in the introduction. After the appropriate formula had been derived for the C_H and S_H generalised projections, the $|k|$ data was collected by photographic Weissenberg techniques and estimated visually as usual. Corrections for Lorentz-polarisation and Tunell effects were applied by hand.

Using the bromine coordinates previously derived, structure factors based on bromine alone were calculated by hand. Those reflexions for which the geometrical part of the structure factor was greater than 1 were used for the projections.(The maximum value of the geometrical structure factor for two bromine atoms per assymmetric unit in a cell of multiplicity four is eight.)

The C_H and S_H fourier series were summed with Beevers-Lipson strips and a modulus function evaluated. This was combined with the 100 electron density projection by means of a minimum function and three-dimensional coordinates derived for the 32 atoms which seemed most probable. Some of these later turned out to be spurious for which the rather bad overlap in the projection must be blamed. Attempts were made to fit the models suggested to this set but this was not very successful. Actually, quite

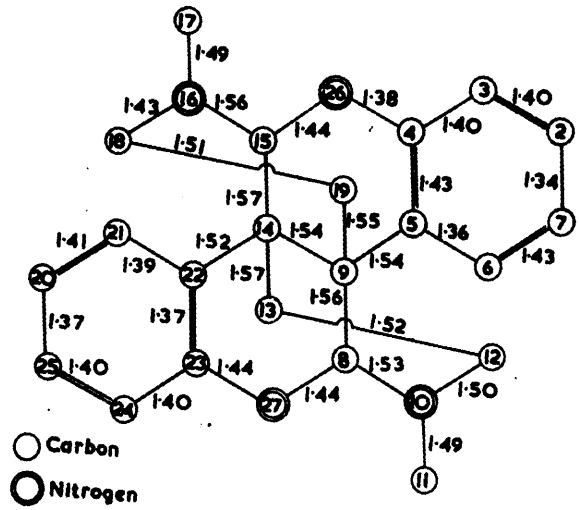
a number of atoms were found in positions close to those in the final structure. A list is given in table 2).

After much work which led only to partial conclusions about the molecule, it was decided that the best approach would be to use three-dimensional methods and the heavy atom technique as the University had then placed an order for a Deuce computer. By means of Weissenberg and multiple film techniques some 2116 reflexions were measured above background. The structure was recognised partially in the first three-dimensional electron density map and refined by fourier methods until all the heavier atoms had been found. The final discrepancy was 9.6% with 18 hydrogen atoms included in the calculation, after three cycles of least squares refinement.

A diagram of the molecule is shown in figure 28).

It will be seen that the structure is not one of those suggested earlier although it appears that this conformation was also considered but the crystal structure was in fact worked out without this information.

The final listing of observed and calculated structure factors is given as table 4). The final positional parameters and anisotropic thermal parameters are given in table 3).



Bond lengths (Å).

Bond angles.

Angles: 5—9—14, 109°.
8—9—19, 113°.
9—14—22, 108°.
13—14—15, 113°.

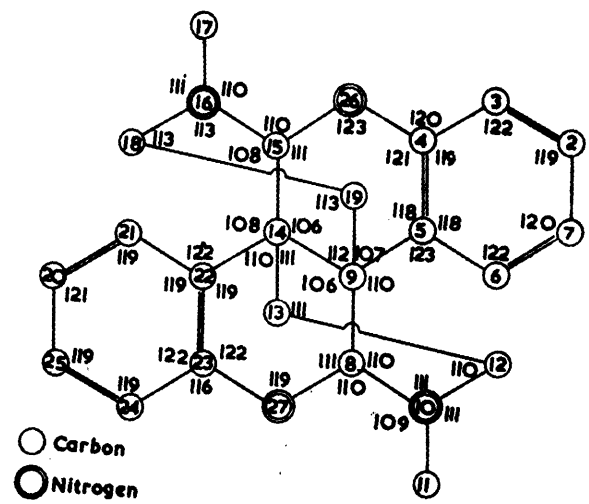


Figure 28.

Table 2.

Atom No.	Coords.(Refinement) x	y	z (Å)	Coords.(Gen. Proj.) x	y	z (Å)
4	1.6	8.0	3.1	1.0	8.1	2.7
5	0.2	8.1	2.9	0.7	8.2	3.2
6	9.3	8.9	1.9	9.5	8.6	1.6
7	0.6	9.6	1.0	0.4	9.4	0.8
9	8.9	7.2	3.7	9.5	7.2	3.6
10	6.6	5.8	3.8	6.6	6.2	3.5
12	7.5	4.6	4.2	8.8	5.3	3.5
13	8.7	4.9	4.9	9.2	4.9	4.9
15	1.3	6.3	4.9	1.1	6.3	4.8
16	0.9	7.0	5.5	0.3	7.2	6.1
17	2.1	7.3	7.0	2.7	7.7	7.5
19	8.6	8.0	5.0	8.4	8.5	5.1
20	2.0	3.9	1.4	0.9	3.9	1.2
22	0.5	5.2	2.8	0.3	4.9	2.5
23	9.5	5.4	1.7	8.7	5.4	1.7
25	1.2	4.1	0.3	1.1	4.5	0.3
26	2.1	7.2	4.1	1.7	7.2	4.2

Although in several cases the agreement is quite good, overlap has prevented the recognition of some atoms which would have allowed the definition of the ring systems and also it must be admitted that the x-coordinate tends only to be approximately correct.

TABLE 3.

Atomic co-ordinates and temperature factors.

Atom	x/a	y/b	z/c	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{23}$	$10^4\beta_{31}$	$10^4\beta_{12}$	B (Å^2)
Br(0)	−0·1147	0·4338	0·5024	158	88	45	12	33	−11	4·2
Br(1)	−0·4787	0·6204	0·2936	127	89	52	11	−12	11	4·2
C(2)	0·2011	0·6732	0·0704	228	92	34	−4	−8	−93	4·5
C(3)	0·2545	0·6158	0·1305	126	92	48	−2	44	−26	4·0
C(4)	0·1672	0·5634	0·1800	146	64	40	8	−12	−55	3·5
C(5)	0·0205	0·5683	0·1680	100	69	37	−28	5	1	3·1
C(6)	−0·0289	0·6265	0·1105	178	70	52	−29	8	11	4·2
C(7)	0·0627	0·6780	0·0598	197	80	37	6	−21	−65	4·1
C(8)	−0·2055	0·4756	0·1728	104	74	44	12	−34	−35	3·4
C(9)	−0·0737	0·5068	0·2202	73	57	38	−9	16	3	2·7
N(10)	−0·2982	0·4120	0·2235	108	72	47	11	−5	−31	3·5
C(11)	−0·4286	0·3918	0·1792	127	92	65	−14	−38	−8	4·5
C(12)	−0·2241	0·3220	0·2454	180	59	48	−23	−30	2	3·9
C(13)	−0·0898	0·3449	0·2893	179	55	34	8	1	5	3·5
C(14)	0·0047	0·4146	0·2406	83	71	40	27	−34	22	3·1
C(15)	0·1394	0·4452	0·2862	158	57	35	−1	5	4	3·3
N(16)	0·0923	0·4972	0·3625	113	83	41	−17	0	9	3·6
C(17)	0·2151	0·5158	0·4141	157	136	29	−11	−8	−28	4·6
C(18)	0·0172	0·5823	0·3462	179	100	37	−18	2	9	4·4
C(19)	−0·1082	0·5655	0·2949	121	70	49	−32	−16	−20	3·6
C(20)	0·2062	0·2758	0·0840	142	92	59	−15	66	36	4·5
C(21)	0·1703	0·3155	0·1572	154	61	43	0	28	−21	3·6
C(22)	0·0488	0·3683	0·1635	122	74	37	9	−20	−17	3·4
C(23)	−0·0334	0·3796	0·0982	138	81	36	−13	−6	54	3·6
C(24)	0·0027	0·3428	0·0245	115	81	48	−10	13	−27	3·7
C(25)	0·1271	0·2920	0·0179	196	69	48	−32	58	−37	4·2
N(26)	0·2223	0·5075	0·2387	111	76	37	4	−27	−43	3·3
N(27)	−0·1667	0·4263	0·1022	94	79	41	4	3	5	3·3
H_2O(28)	−0·3944	0·4182	0·3848	118	105	37	3	5	−2	3·9
H_2O(29)	−0·6405	0·2772	0·3483	187	146	52	−5	−7	51	5·7
H(2)	0·270	0·719	0·040	—	—	—	—	—	—	4·0
H(3)	0·358	0·614	0·130	—	—	—	—	—	—	4·0
H(6)	−0·133	0·623	0·111	—	—	—	—	—	—	4·0
H(7)	0·017	0·719	0·017	—	—	—	—	—	—	4·0
H(8)	−0·241	0·541	0·170	—	—	—	—	—	—	4·0
H(12)	−0·283	0·297	0·293	—	—	—	—	—	—	4·0
H′(12)	−0·208	0·275	0·203	—	—	—	—	—	—	4·0
H(13)	−0·029	0·283	0·290	—	—	—	—	—	—	4·0
H′(13)	−0·125	0·391	0·335	—	—	—	—	—	—	4·0
H(15)	0·191	0·385	0·286	—	—	—	—	—	—	4·0
H(18)	0·071	0·628	0·316	—	—	—	—	—	—	4·0
H′(18)	−0·008	0·603	0·406	—	—	—	—	—	—	4·0
H(19)	−0·158	0·524	0·328	—	—	—	—	—	—	4·0
H′(19)	−0·179	0·628	0·295	—	—	—	—	—	—	4·0
H(20)	0·291	0·238	0·083	—	—	—	—	—	—	4·0
H(21)	0·237	0·303	0·198	—	—	—	—	—	—	4·0
H(24)	−0·083	0·345	−0·019	—	—	—	—	—	—	4·0
H(25)	0·137	0·258	−0·038	—	—	—	—	—	—	4·0

Tables 3) and 4) and figure 28) are taken from the final paper on Calycanthine dihydrobromide by Hamor & Robertson (1962). The structure was originally reported by Hamor, Robertson, Shrivastava & Silverton (1960).

TABLE 4.

Observed and calculated structure factors.

h	k	l	$\|F_o\|$	$\|F_c\|$	α°
0	0	2	117	142	180
		4	100	118	0
		6	92	97	0
		8	53	44	0
		10	120	122	0
		12	30	27	0
		14	75	67	0
		18	27	26	0
		20	25	22	0
0	1	1	11	0	270
		2	23	37	270
		3	88	97	270
		4	50	59	270
		5	71	61	90
		6	24	34	90
		7	86	81	270
		8	60	56	270
		10	22	19	90
		11	10	8	270
		12	10	10	270
		13	19	18	270
		14	52	49	270
		15	22	20	270
		16	46	45	90
		17	35	35	270
		18	43	37	270
0	2	0	154	189	0
		1	24	39	180
		2	58	50	180
		3	17	9	0
		4	60	54	0
		6	45	56	0
		7	65	57	180
		8	71	63	0
		9	58	57	0
		10	65	58	0
		11	43	44	180
		12	29	28	0
		13	47	53	0
		14	21	19	0
		15	14	13	180
		16	17	16	0
		17	17	16	180
		18	22	19	0
		20	9	7	0
		21	9	10	180
0	3	1	90	97	270
		2	74	64	90
		3	176	185	270
		4	145	138	90
		5	5	4	270
		6	86	84	270
		7	150	151	270
		8	53	55	90
		9	42	39	270
		10	17	21	270
		11	61	54	270
		13	40	36	270
		14	14	15	90
		15	30	23	270
		17	52	45	270
		18	10	12	90
		21	7	8	270
0	4	0	192	161	180
		1	58	55	180
		2	78	80	0
		3	42	34	0
		4	21	20	180
		5	45	40	0
		6	13	20	180
		7	76	61	180
		8	26	29	0
		9	21	19	180
		10	75	68	180
		12	42	45	0
		13	21	19	180
		14	9	14	180
		15	21	22	180
		17	11	10	180
		20	13	13	180
		21	5	6	180
0	5	1	85	82	270
		2	10	7	270
		3	20	25	270
		4	48	48	90
		5	176	155	270
		6	114	100	270
		7	65	58	270
		8	36	36	90
		9	61	56	270
		11	35	37	270
		12	9	8	90
		13	27	24	270
		14	20	20	90
		15	21	24	270
		16	18	16	270
		17	17	12	270
		18	16	12	90
		19	21	20	270
		20	11	12	270
0	6	0	80	82	180
		1	79	79	0
		2	32	34	180
		3	35	36	180
		4	24	31	180
		6	78	69	180
		8	40	39	180
		9	16	19	180
		10	79	65	180
		11	46	45	0
		12	19	21	180
		13	33	34	180
		14	10	12	180
		15	14	13	0
		16	15	14	180
		17	19	18	180
		20	17	14	180
0	7	1	37	39	270
		2	16	20	90
		3	29	32	90
		4	13	14	270
		5	85	77	270
		6	41	38	90
		7	80	73	90
		8	12	15	270
		9	32	31	270
		10	14	14	90
		11	23	22	270
		12	20	19	90
		13	14	14	270
		14	43	53	180
		15	19	21	180
		16	57	52	180
		17	37	32	0
		18	45	49	180
		19	15	14	0
		20	57	60	180
		21	10	8	180
		22	29	27	180
		23	20	20	180
		24	11	11	270
		25	16	16	90
		26	38	38	90
		27	21	23	90
		28	19	19	90
		29	16	19	270
		30	11	12	0
		31	15	16	90
		32	13	14	90
		33	16	16	90
		34	10	10	270
		35	11	12	0
		36	11	11	0
		37	8	8	180
		38	6	6	90
		39	6	11	0
		40	8	12	180
1	0	1	69	89	90
		2	11	24	180
		3	94	99	90
		4	9	9	180
		5	5	10	270
		6	20	22	180
		7	24	27	270
		8	64	68	90
		9	34	32	0
		10	15	15	131
		11	28	26	52
		12	40	45	283
		13	19	19	319
		14	12	14	138
		15	20	18	33
		16	25	22	270
		17	11	7	81
		18	11	9	270
		19	9	8	67
		20	8	8	163
1	7	0	42	47	270
		1	54	56	171
		2	40	45	249
		3	28	28	180
		4	56	63	329
		5	77	89	164
		6	43	43	102
		8	54	55	290
		9	55	56	192
		10	23	25	230
		11	21	22	213
		12	25	25	235
		13	19	20	157
		14	20	20	315
		15	24	22	180
		16	24	23	229
		18	12	12	319
		19	22	21	184
		20	9	10	251
1	8	1	58	62	258
		2	13	15	31
		3	54	56	113
		4	19	22	91
		5	13	14	264
		6	18	19	262
		7	32	36	256
		8	14	15	7
		9	35	37	85
		10	24	24	147
		11	14	18	242
		13	22	26	99
		16	7	8	89
		19	6	7	66
1	9	0	37	37	270
		1	36	40	193
		2	34	38	301
		4	27	30	228
		5	67	70	105
		6	20	21	328
		7	25	26	35
		8	46	50	242
		9	50	51	176
		10	30	28	341
		11	11	11	185
		12	14	19	203
		13	8	10	144
		14	8	9	247
		15	23	23	166
		16	14	15	320
		17	9	9	32
		19	13	19	180
1	10	0	24	24	270
		1	10	22	226
		2	50	57	87
		3	14	17	132
		4	20	20	104
		5	25	30	176
		6	9	11	75
		7	36	40	203
		8	44	50	93
		9	19	23	126
		11	19	16	243
		12	28	30	90
		15	10	10	177
		16	13	13	87
1	11	2	12	10	329
		3	19	21	184
		4	16	21	171
		6	21	25	344
		8	14	17	176
		10	19	19	8
		16	14	13	344
		17	7	9	162
1	12	0	16	16	90
		1	35	40	119
		2	30	32	83
		3	35	34	232
		4	22	24	94
		5	14	17	152
		6	8	10	79
		7	12	16	144
		8	17	20	90
		9	13	17	220
		10	14	13	48
		11	7	10	147
		12	12	12	82
		13	19	21	243
		14	11	11	70
		15	10	11	142
		16	6	7	58
1	13	0	11	11	90
		1	21	24	39
		2	11	13	107
		3	8	9	209
		4	11	13	34
		5	20	29	25
		8	12	15	54
		9	14	17	0
		10	11	11	102
		14	8	8	81
		15	13	17	12
1	14	0	19	24	90
		1	22	19	105
		2	8	9	292
		3	13	14	233
		4	11	12	65
		5	11	7	224
		6	10	10	120
		7	12	12	152
		10	11	14	81
		13	6	7	199
1	15	0	8	6	90
		1	8	10	60
		2	21	20	124
		3	24	21	344
		4	7	8	86
		7	10	14	347
2	0	0	113	120	0
		1	133	132	90
		2	71	54	180
		3	119	124	90
		4	45	45	0
		5	151	156	90
		6	84	72	0
		7	101	92	90
		8	27	30	180
		10	57	59	0
		11	67	62	90
		12	46	48	180
		13	64	60	90
		14	18	24	0
		15	32	29	90
		16	9	12	180
		17	37	31	90
		19	12	13	90
		20	13	15	0
		21	9	12	90
2	1	0	54	56	0
		1	82	65	21
		2	63	63	65
		3	68	56	271
		4	116	108	292
		5	77	66	94
		6	46	51	72
		7	39	39	312
2	2	0	22	24	0
		1	115	114	186
		2	8	7	129
		3	160	129	90
		4	69	62	262
		5	95	82	101
		6	29	23	51
		7	53	48	118
		8	13	9	37
		9	52	59	38
		11	61	62	134
		12	16	15	277
		13	32	30	24
		14	9	11	7
		15	22	27	137
		17	27	26	70
		18	10	12	270
		19	9	8	58
		21	18	19	130
2	3	0	79	95	0
		1	33	35	105
		2	146	131	351
		3	92	82	268
		4	121	99	26
		5	62	58	104
		6	101	96	326
		7	58	63	238
		8	76	76	46
		9	16	19	31
		10	55	65	352
		12	57	53	8
		14	24	28	27
		15	13	16	102
		16	36	35	310
2	4	0	176	179	180
		1	11	9	181
		2	114	98	322
		3	10	12	112
		4	40	42	128
		5	25	26	305
		7	34	32	196
		8	40	44	351
		9	15	15	55
		10	50	52	198
		11	18	19	177
		12	22	26	295
		13	13	13	293
		14	12	12	251
		15	17	16	188
		16	14	15	223
		17	7	6	0
2	5	0	46	46	0
		1	75	67	244
		2	95	92	347
		3	58	65	23
		4	41	46	62
		5	42	41	275
		6	105	102	330
		7	31	31	130
		8	67	71	35
		9	23	22	291
		10	32	32	314
		11	21	21	227
		12	61	61	0
		14	28	26	75
		16	36	33	313
2	6	0	37	36	180
		1	49	61	303
		2	47	46	317
		3	68	69	219
		4	49	46	104
		5	80	78	289
		6	29	32	265
		7	51	51	275
		8	17	20	95
		9	45	49	221
		10	9	9	340
		11	46	50	323
		12	25	26	189
		13	36	43	222
		14	10	11	64
		15	20	19	203
		17	14	14	274
		19	9	8	194
		20	9	9	230
2	7	0	20	21	0
		1	30	30	259
		2	26	28	346
		3	60	63	85
		4	36	41	200
		5	51	52	252
		6	31	33	88
		7	25	29	109
		8	9	11	300
		9	8	11	255
		10	12	12	93
		11	11	14	188
		12	20	19	336
		13	11	11	150
		14	12	12	242
		16	15	16	30
		19	14	12	215
2	8	0	55	50	0
		1	80	79	285
		2	54	57	187
		3	30	35	279
		4	12	11	41
		5	63	69	275
		6	12	10	241
		7	36	34	286
		8	23	27	194
		9	35	39	255
		10	33	35	9
		11	29	23	290
		12	29	30	162
		13	34	28	261
		15	37	32	297
		16	11	11	176
		17	11	9	267
		19	10	12	260
2	9	0	10	13	180
		1	17	17	52
		2	41	42	156
		3	12	15	228
		4	30	32	244
		5	20	24	84
		6	38	39	117
		7	12	13	252
		8	14	20	209
		9	11	13	112
		10	16	18	120
		11	9	11	332
		12	18	19	174
		13	18	18	127
		15	10	7	212
2	10	1	32	31	228
		2	28	29	112
		3	21	25	344
		5	23	23	236
		6	15	15	90
		7	12	16	231
		8	13	14	213
		9	26	31	327
		11	26	28	109
		12	21	20	340
		13	15	14	254
		16	7	7	82
2	11	0	35	37	180
		2	38	44	176
		3	23	26	298
		4	21	27	168
		5	21	27	106
		6	36	39	209
		7	12	18	270
		8	20	18	156
		9	17	20	66
		10	14	19	185
		12	23	24	182
		14	10	13	147
		15	7	8	93
		16	14	15	206
2	12	0	23	26	180
		2	21	24	19
		3	14	14	10
		4	14	16	234
		5	11	16	96
		6	11	12	38
		7	16	15	225
		8	21	20	170
		9	11	9	36
		13	8	6	26
2	13	0	9	13	180
		2	9	14	201
		3	11	17	53
		4	17	21	119
		6	23	27	224
		7	12	11	111
		8	15	15	174
		9	12	11	350
		10	12	13	204
		12	9	9	192
		13	9	8	7
		14	7	7	144
2	14	1	18	21	45

TABLE 4. · (*Continued*).

h	k	l	$\|F_o\|$	$\|F_c\|$	α°
		3	19	20	127
		5	27	28	67
		6	10	8	43
		7	9	12	85
		8	12	11	322
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		11	16	17	49
		13	8	9	137
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		5	9	11	251
		7	17	16	69
		9	11	10	305
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		3	9	14	122
		5	10	10	59
		7	15	15	97
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		4	39	41	0
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		6	61	61	180
		7	33	28	270
		8	27	29	0
		9	81	82	90
		10	10	10	0
		11	42	44	270
		13	27	31	90
		14	13	15	0
		15	10	13	270
		17	9	8	270
		18	17	15	0
		19	8	10	90
		20	6	8	180
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		2	85	75	35
		3	43	35	101
3	1	4	110	101	122
		5	124	120	184
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		7	37	32	354
		8	56	51	119
		9	80	79	192
		10	86	83	83
		11	16	16	235
		12	16	15	60
		13	14	14	168
		14	30	33	112
		15	30	33	200
		16	25	23	47
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		18	18	18	136
		19	17	19	105
		20	13	15	56
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		5	16	18	27
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		7	90	83	355
		8	69	65	81
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		11	18	20	326
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		13	29	31	2
		15	11	9	22
		16	14	14	72
		17	23	24	9
		18	23	19	69
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		1	41	45	270
		2	42	37	60
		3	61	52	152
		4	87	70	112
		5	47	45	321
		6	23	25	346
		7	42	43	185
		8	51	49	142
		9	16	20	33
		10	8	12	306
		11	26	25	249
		12	39	41	54
		13	24	31	154
		14	24	27	181
		15	21	18	266
		16	17	14	32
		17	9	10	207
		18	15	12	143
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		7	69	71	25
		8	41	42	135
		9	53	58	311
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		11	46	47	53
		12	35	32	137
		13	53	51	304
		14	16	20	101
		15	22	19	27
		17	25	25	3
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		5	90	88	350
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		12	11	12	30
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		16	20	21	249
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		3	44	39	14
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		5	57	60	4
		6	24	27	97
		7	17	17	46
		8	21	22	208
		9	37	40	321
		10	37	49	74
		11	39	38	51
		12	14	16	222
		13	10	11	325
		14	30	26	107
		15	14	14	345
		16	10	9	229
		17	8	8	3
		19	7	8	337
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		1	15	13	161
		2	80	74	257
		3	55	59	353
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		5	22	24	356
		6	67	67	235
		7	31	33	16
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		10	22	24	230
		11	15	16	59
		12	29	30	249
		13	33	31	319
		14	24	23	334
		15	12	9	27
		16	13	13	270
		17	24	23	354
		18	27	30	256
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		3	48	49	121
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		5	17	17	302
		6	23	22	202
		7	20	23	219
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		9	14	18	126
		10	11	16	281
		12	12	15	235
		13	20	20	93
		16	11	12	173
3	9	1	13	17	303
		2	48	51	277
		3	49	54	353
		4	27	27	217
		5	14	15	78
		6	44	47	296
		7	35	40	0
		8	29	33	229
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		11	14	11	36
		12	19	19	246
		13	17	19	165
		14	18	16	248
		16	10	11	290
		17	13	13	32
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		3	19	21	109
		4	17	22	234
		5	19	24	175
		6	18	22	263
		7	9	12	234
		8	36	31	181
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		11	17	16	189
		13	14	14	195
		14	20	20	272
		15	11	12	179
3	11	0	11	12	270
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		2	16	18	347
		3	16	15	159
		4	25	26	188
		5	11	11	24
		6	36	31	3
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		14	8	9	215
3	12	0	15	20	270
		1	30	33	132
		2	12	10	269
		3	31	32	230
		4	13	18	242
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		6	9	10	6
		7	21	21	138
		8	11	9	297
		9	10	12	200
		10	19	21	282
		11	19	21	137
		13	13	13	233
		14	12	11	293
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		3	22	23	174
		4	19	19	91
		7	22	24	161
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		12	9	10	83
		13	12	12	194
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		1	11	11	118
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		3	17	18	203
		5	10	8	335
		7	22	21	165
		8	15	16	264
		10	8	9	55
		11	9	10	200
3	15	0	12	14	90
		1	12	11	150
		4	23	22	51
		5	11	10	187
		6	9	11	161
		8	11	11	64
		10	10	11	120
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		0	12	11	90
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		4	38	34	180
		5	8	1	270
		6	101	95	180
		7	41	43	90
		8	68	76	180
		9	28	23	270
		10	31	30	180
		11	37	32	90
		12	42	41	180
		14	26	28	180
		16	27	26	180
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		18	20	26	180
		20	7	8	180
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		3	37	26	307
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		5	94	86	118
		6	37	37	87
		7	38	40	330
		8	15	18	229
		9	44	44	82
		10	20	21	337
		11	20	15	47
		12	26	22	137
		13	12	11	82
		14	21	22	345
		15	18	16	93
		16	21	24	111
		17	9	8	303
		18	7	11	278
		19	12	14	83
		20	8	8	50
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		3	25	21	53
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		6	50	48	130
		7	21	20	130
		8	45	44	216
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		10	46	46	183
		11	44	47	137
		12	9	9	139
		13	39	41	11
		14	26	25	207
		15	7	12	104
		16	18	18	169
		17	9	9	344
		18	14	15	215
		19	6	4	42
		20	9	9	156
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		2	22	20	208
		3	68	63	40
		4	85	82	47
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		6	39	39	291
		7	12	12	108
		8	13	19	57
		9	82	75	83
		10	19	19	330
		11	29	31	99
		12	11	14	160
		13	26	24	69
		14	29	30	23
		15	33	32	91
		16	9	9	251
		17	10	8	75
		18	6	6	74
		19	18	20	85
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		1	16	14	160
		2	60	58	22
		3	11	14	216
		4	17	12	234
		5	19	17	48
		6	18	14	211
		7	34	33	293
		8	15	15	29
		9	24	20	75
		10	30	27	223
		12	36	37	0
		14	20	19	193
		15	9	9	50
		16	12	13	320
		17	11	11	317
		18	10	8	309
		19	9	8	64
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		1	62	63	133
		2	42	43	331
		3	63	63	79
		4	43	42	76
		5	7	6	156
		6	41	41	286
		7	75	72	97
		8	22	22	25
		9	28	29	51
		11	34	31	108
		12	22	21	358
		13	37	34	89
		15	25	21	134
		16	20	17	294
		17	28	26	86
		19	5	5	97
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		2	70	68	334
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		4	50	55	25
		6	32	36	315
		7	20	21	201
		8	33	36	12
		9	31	32	197
		10	35	34	353
		11	28	29	354
		12	25	26	358
		13	25	26	198
		16	20	21	326
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		2	23	29	9
		3	43	44	113
		4	35	35	244
		5	22	23	243
		6	32	30	52
		7	38	42	61
		8	33	33	283
		9	9	10	203
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		11	7	6	124
		12	12	11	309
		13	18	14	156
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		17	11	11	88
		18	11	14	299
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		1	25	25	204
		2	13	13	34
		3	9	9	1
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		5	25	26	233
		6	32	34	11
		7	23	24	52
		8	16	17	351
		9	36	40	280
		10	59	67	4
		11	7	7	51
		14	31	30	15
		15	9	9	260
		16	8	8	354
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		1	17	22	330
		2	6	7	121
		3	33	35	239
		4	31	28	273
		5	18	19	170
		6	16	19	107
		7	36	37	306
		8	18	21	261
		9	15	17	219
		10	14	15	22
		11	10	10	313
		12	16	14	155
		13	20	20	222
		16	13	13	81
		17	13	16	272
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		1	30	33	200
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		3	29	29	19
		4	38	40	311
		5	29	26	221
		6	23	22	85
		9	17	15	279
		10	19	20	24
		11	24	23	159
		12	8	3	340
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		14	11	12	349
		16	7	5	8
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		2	7	10	171
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		4	7	9	124
		5	9	12	262
		6	13	14	222
		7	47	44	263
		8	13	13	134
		9	19	17	272
		10	9	9	310
		11	10	9	280
		12	12	12	157
		13	17	17	281
		14	6	5	95
		15	11	9	221
4	12	0	23	23	180
		6	12	11	133
		7	13	12	259
		9	8	7	77
		10	24	24	176
		11	7	8	144
		12	16	14	12
		13	8	7	280
		14	8	9	173
4	13	0	9	10	180
		1	17	18	218
		3	27	21	335
		4	20	20	118
		5	21	20	240
		6	19	17	276
		7	7	8	232
		8	11	10	111
		9	18	15	316
		10	6	7	216
		11	7	9	242
		12	6	3	138
4	14	0	27	25	180
		1	16	15	12
		2	11	10	208
		3	12	11	174
		4	15	15	162
		5	10	7	30
		8	11	13	198
		10	17	17	184
		11	10	11	26
4	15	5	7	10	268
		6	6	7	97
		7	9	9	92
		8	6	3	180
4	16	0	6	3	180
		2	10	15	179
		3	10	11	117
		4	5	8	162
		6	12	9	201
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		3	102	83	90
		4	36	32	0
		5	12	8	270
		6	36	36	180
		7	15	10	270
		8	31	29	0
		9	42	38	90
		10	12	16	180
		11	45	50	270
		12	13	15	0
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		1	108	91	103
		2	84	71	270
		3	18	20	78
		4	30	32	167
		5	105	105	103
		6	37	35	328
		7	15	10	177
		8	46	48	245
		9	50	51	152
		10	20	18	42
		11	40	42	212
		12	41	37	281
		13	15	16	157
		14	11	13	107
		15	30	26	104
		16	22	19	312
		17	12	11	159
		19	12	13	177
		20	7	10	335
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		1	41	39	180
		2	109	89	82
		3	12	7	134
		4	23	20	95
		5	49	51	181
		6	36	39	90
		7	13	10	27
		8	43	47	82
		9	29	28	171
		10	7	9	196
		12	43	44	92
		13	22	26	99
		14	16	17	98
		15	25	25	197
		16	8	14	78
		18	19	17	89
		19	9	9	146
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		1	33	31	275
		2	37	33	34
		3	34	34	161
		4	40	41	206
		5	8	9	316
		6	47	45	359
		7	62	62	188
		8	28	29	204
		9	12	12	44
		10	25	27	312
		11	17	17	247
		12	15	12	354
		13	12	12	160
		14	7	12	205
		16	17	15	11
		17	18	20	176
5	4	0	55	55	90
		1	45	46	104
		2	57	57	68
		3	58	53	244
		4	60	59	123
		5	34	30	144
		6	67	64	57
		7	30	31	151
		8	38	42	113
		9	47	45	249
		10	18	18	47
		11	23	23	138
		12	44	38	96
		13	23	22	243
		14	23	23	113
		15	15	15	145
		16	17	18	32
		17	9	7	108
		18	14	14	114
		19	7	9	242
5	5	0	10	4	270
		1	34	35	33
		2	33	32	109
		3	28	25	292
		4	12	10	328
		5	57	57	357
		6	26	26	95
		7	20	20	136
		8	45	41	49
		9	30	33	347
		10	20	18	300
		11	26	26	17
		12	22	22	72
		13	14	12	257
		14	10	10	6
		15	18	19	33
		17	8	7	237
		18	11	11	36
		19	8	12	357
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		1	6	3	257
		2	12	12	7
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		4	52	49	99
		5	24	22	56
		6	29	32	99
		7	39	43	176
		8	10	11	154
		9	21	19	323
		10	35	40	81
		11	11	11	203
		13	14	13	196
		14	22	21	80
		15	8	6	341
		16	8	8	73
		17	12	12	175
		18	9	6	158
5	7	0	29	31	90
		1	38	40	49
		2	23	22	152
		3	56	55	339
		4	34	36	31
		5	20	20	30
		6	30	29	172
		7	30	30	10
		8	22	20	35
		9	18	17	310
		10	32	35	115
		11	32	36	12
		13	27	26	334
		14	16	14	49
		15	8	9	28
		16	6	8	166
		17	16	15	347
		18	11	13	49
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		1	37	39	282
		2	14	16	245
		3	16	15	91
		4	29	32	336
		5	19	18	12
		6	20	20	232
		7	15	14	261
		8	9	9	242
		9	7	9	18
		10	11	9	127
		11	14	13	285
		13	9	9	102
		15	12	10	296
		16	9	10	165
		17	6	4	236
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		3	37	41	13
		4	17	19	118
		5	16	16	4
		6	8	11	91
		7	28	31	339
		8	10	10	201
		9	11	12	344
		10	24	24	92
		11	17	16	6
		12	10	9	204
		13	22	20	13
		14	11	11	121
		15	7	6	293
		16	5	2	158
5	10	0	46	45	270
		3	16	22	354
		4	20	25	267
		6	28	30	268
		7	27	28	341
		8	7	8	70
		9	9	9	189
		10	31	28	268
		11	11	11	309
		13	13	15	5
		14	28	27	281
		15	10	11	270
5	11	0	16	15	309
		1	16	15	309
		3	18	17	109
		4	9	9	188
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		10	14	13	332
		11	7	6	303
		12	7	8	106
		13	13	13	97
		14	8	8	199
		15	5	7	308
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TABLE 4. (*Continued*).

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		6	29	28	291
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		8	7	8	235
		10	9	12	280
		11	6	8	55
		12	13	11	241
		13	9	7	22
5	13	0	26	23	270
		1	12	12	137
		2	11	11	161
		3	20	21	180
		4	13	13	328
		6	8	8	197
		7	16	17	176
		10	12	11	260
		11	7	8	218
		12	4	4	212
5	14	2	17	19	270
		6	7	9	313
		8	13	10	260
		9	6	7	2
		10	4	3	24
5	15	1	11	11	171
		2	8	7	212
		4	8	8	342
		5	11	11	178
		6	7	10	214
		7	7	9	142
		8	6	8	322
5	16	0	6	8	90
		1	6	6	285
		3	10	8	153
6	0	0	27	28	0
		1	78	67	270
		2	55	46	180
		3	25	25	270
		4	7	7	180
		5	88	83	270
		6	5	5	180
		7	23	23	270
		8	42	38	180
		9	57	59	270
		10	7	8	0
		11	37	37	270
		12	15	11	180
		13	8	12	270
		14	13	9	180
		15	31	31	270
		16	17	18	180
		18	5	6	180
		19	15	21	270
6	1	0	18	15	0
		1	63	57	35
		2	38	37	185
		3	42	35	270
		4	28	27	277
		5	38	32	62
		6	57	47	121
		7	18	20	309
		8	25	28	202
		9	34	32	133
		10	16	13	73
		11	7	8	61
		12	27	26	107
		13	14	14	107
		15	13	13	46
		16	17	16	107
		17	8	8	255
		18	9	7	193
		19	7	9	129
6	2	0	20	22	180
		1	65	57	227
		2	40	37	117
		3	57	50	319
		4	53	53	260
		5	32	24	306
		6	47	41	111
		7	21	23	216
		8	36	35	236
		9	44	39	342
		10	23	23	97
		11	35	36	249
		13	26	24	318
		14	16	16	207
		15	17	17	275
		16	10	12	95
		17	11	7	307
		18	10	10	268
		19	7	9	300
6	3	1	53	48	129
		2	78	77	195
		3	11	12	352
		4	53	53	159
		5	27	22	69
		6	37	38	181
		7	29	28	184
		8	53	53	173
		9	42	46	65
		10	10	10	134
		12	38	36	181
		13	19	22	12
		14	19	20	123
		15	16	15	125
		16	24	23	193
		17	6	8	323
		18	14	14	164
6	4	0	47	50	180
		1	9	10	78
		2	39	40	26
		3	20	20	234
		4	26	22	192
		5	38	34	39
		6	26	22	65
		7	36	35	227
		8	15	14	290
		9	37	31	87
		10	31	27	139
		11	18	13	345
		12	15	16	346
		13	8	8	288
		14	11	10	189
		15	16	15	62
		16	13	12	50
		17	10	11	291
		18	3	3	21
6	5	0	41	42	180
		1	37	35	173
		2	35	37	210
6	13	0	10	9	0
		2	18	19	324
		3	10	10	302
		4	12	10	81
		6	9	10	308
		7	9	8	197
		8	11	12	40
		9	8	7	310
		11	6	10	205
6	14	1	13	14	314
		3	17	18	249
		4	12	13	113
		5	10	9	307
		8	8	8	247
		9	9	10	287
		10	6	7	233
6	15	0	10	10	180
		1	4	3	353
		2	9	9	342
		3	7	6	155
		4	8	7	107
		6	8	9	53
7	0	1	39	34	270
		2	16	13	180
		3	17	15	90
		4	40	38	0
		5	10	9	270
		6	59	46	180
		7	5	4	90
		8	7	7	180
		9	27	26	90
		13	22	21	90
		16	17	17	180
		18	3	0	0
7	1	0	7	11	270
		1	36	30	266
		2	73	58	273
		3	38	36	35
		4	41	36	290
		5	5	3	73
		6	51	48	280
		7	20	19	356
		8	29	30	235
		9	8	8	91
		11	8	11	282
		12	39	40	280
		13	24	23	47
		14	11	10	282
		16	15	18	286
		17	11	14	14
		18	9	14	251
7	2	0	56	56	270
		1	57	48	177
		2	9	11	62
		3	5	8	146
		4	33	38	278
		5	69	58	181
		6	5	4	181
		7	18	17	3
		9	41	46	104
		10	25	28	261
		11	25	24	108
		12	13	13	120
		13	12	13	268
		14	15	19	181
		15	18	19	181
		16	9	7	211
7	3	0	29	27	270
		1	16	16	301
		2	11	11	3
		3	26	24	135
		4	31	30	228
		5	53	47	358
		6	20	19	330
		7	13	10	159
		8	7	5	326
		9	20	23	23
		10	33	34	272
		11	12	16	252
		12	14	12	55
		13	24	23	99
		14	8	11	232
		16	11	11	343
7	4	0	25	25	270
		1	44	47	187
		2	13	11	94
		3	24	24	214
		4	40	41	214
		5	34	31	175
		6	47	44	14
		7	41	37	157
		8	23	22	244
		9	27	30	219
		10	13	17	277
		11	32	35	148
		13	22	22	229
		14	8	8	266
		16	6	8	343
		17	13	14	176
7	5	0	12	10	270
		1	42	43	87
		2	36	33	89
		3	39	37	210
		4	17	17	22
		5	23	22	349
		6	28	29	86
		7	45	44	158
		8	26	27	66
		9	9	11	322
		10	11	12	230
		11	19	16	113
		12	28	25	77
		13	5	5	205
		14	6	5	343
		15	10	10	110
		16	7	9	84
7	6	0	19	18	90
		1	43	43	242
		2	23	29	246
		3	34	37	160
		4	6	6	192
		5	13	14	306
		6	23	19	12
		7	46	48	170
		8	17	20	276
		9	5	5	324
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		11	19	20	152
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		13	12	13	190
		16	5	3	340
7	7	0	53	50	90
		1	33	29	115
		2	11	12	122
		3	12	13	226
		4	19	22	85
		5	9	10	178
		6	20	29	114
		7	9	8	99
		8	17	18	70
		9	20	19	226
		10	21	24	100
		11	12	16	122
		12	8	8	84
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		14	17	19	58
		15	16	17	175
		16	7	14	128
7	8	0	5	6	90
		1	39	37	265
		2	12	14	242
		3	16	18	83
		4	22	24	24
		5	7	6	348
		6	13	19	166
		7	8	6	273
		8	19	20	10
		9	9	12	30
		10	13	13	143
		11	15	13	209
		14	10	11	341
		15	9	10	273
7	9	0	50	59	90
		1	22	22	235
		2	12	13	343
		4	22	23	108
		5	14	15	198
		6	20	20	175
		7	7	9	296
		8	9	11	124
		9	7	9	137
7	10	0	24	24	92
		1	11	9	262
		2	14	12	15	83
		3	15	19	343
		4	23	22	98
		5	3	18	24	6
		6	4	6	7	321
		7	5	9	8	212
		8	6	7	5	162
		9	24	27	358
		10	8	10	11	66
		11	11	13	340
		12	9	11	75
		13	5	7	4
7	11	1	19	20	273
		2	8	9	35
		3	7	9	89
		5	7	7	18
		6	10	7	36
		7	9	10	240
		8	10	7	153
		9	5	7	77
		11	9	10	257
		12	3	5	80
7	12	0	5	6	270
		1	13	15	30
		2	8	10	69
		3	11	13	338
		4	14	15	159
		5	6	9	335
		6	12	13	19
		7	21	21	12
		8	13	14	140
		9	6	8	330
		11	3	9	18
7	13	0	19	21	270
		2	7	8	164
		4	11	11	300
		6	13	13	224
		8	4	6	353
		9	2	6	343
7	14	1	4	6	7
		5	6	11	13
		6	6	7	52
7	15	1	3	8	87
8	0	0	47	51	0
		1	33	25	270
		2	14	18	0
		4	41	44	0
		5	45	40	270
		6	31	34	0
		7	33	34	90
		8	31	35	0
		9	56	49	270
		10	34	31	0
		11	8	8	270
		14	20	17	0
		15	16	17	270
8	1	0	26	22	0
		1	33	28	340
		2	37	34	138
		3	42	41	183
		4	27	27	258
		5	11	8	133
		6	22	20	103
		7	33	39	320
		8	22	22	224
		9	28	22	187
		10	16	16	349
		11	8	11	301
		12	15	14	180
		13	23	22	212
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8	2	0	17	20	0
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		2	23	26	42
		3	20	20	304
		4	30	29	301
		5	27	24	314
		6	32	29	66
		7	12	13	213
		8	12	14	324
		9	20	20	310
		10	21	20	55
		11	11	11	178
		12	10	11	6
		13	8	10	322
		14	14	14	331
		16	14	16	49
8	3	0	23	26	0
		1	40	41	231
		2	46	43	191
		3	37	36	300
		4	11	12	148
		5	14	14	238
		6	7	10	209
		7	38	35	270
		8	21	23	168
		9	17	20	261
		10	14	14	56
		11	18	19	248
		12	18	22	168
		13	16	17	300
		15	8	10	213
		16	7	9	191
8	4	0	26	26	180
		1	22	23	105
		2	12	12	337
		3	33	33	257
		4	8	9	169
		5	25	25	92
		6	8	6	88
		7	29	28	248
		9	17	18	92
		10	14	15	138
		12	10	10	29
		14	7	7	197
		15	7	11	107
		16	8	9	100
8	5	0	11	10	180
		1	39	39	234
		2	8	6	251
		3	26	27	312
		4	32	30	154
		5	29	28	272
		6	14	14	231
		7	11	11	212
		8	9	9	121
		9	23	25	300
		10	18	17	188
		11	14	14	264
		12	8	11	200
		13	17	19	325
		14	13	13	159
		15	11	14	242
8	6	0	32	33	180
		1	28	29	40
		2	15	18	238
		3	8	9	184
		4	23	24	128
		5	10	11	85
		6	22	26	229
		7	8	7	39
		8	23	25	121
		9	16	13	119
		10	7	8	189
		11	12	12	31
		12	10	11	189
		13	7	9	142
		14	12	15	146
		15	4	6	62
8	7	0	40	43	180
		1	6	7	15
		2	18	20	352
		3	8	7	149
		4	15	14	210
		5	19	16	296
		6	8	8	97
		10	14	13	180
		11	15	17	346
		14	7	9	170
8	8	0	12	13	180
		1	7	7	49
		2	15	20	178
		3	21	25	86
		4	16	20	161
		5	7	8	303
		6	17	19	198
		7	19	24	80
		8	17	20	173
		10	8	10	219
		11	6	6	51
		12	14	18	187
		13	8	11	102
8	9	1	8	9	90
		3	8	9	142
		4	17	16	326
		5	14	16	71
		6	7	9	77
		7	8	10	15
		8	6	4	326
		9	15	17	117
		11	11	14	16
8	10	0	7	8	180
		1	10	13	149
		2	8	11	125
		3	7	7	74
		4	20	23	243
		6	9	13	117
		7	7	6	105
		8	8	9	251
		9	8	8	47
		10	7	6	173
8	11	0	13	16	0
		1	10	14	183
		3	13	12	60
		4	16	18	10
		5	12	16	99
		9	12	17	62
		10	8	12	358
8	12	2	8	9	90
		3	7	11	280
		4	8	9	268
		5	6	8	49
		7	6	9	238
		8	5	6	335
8	13	0	5	4	180
		1	8	12	142
		2	6	9	347
		3	6	8	74
		5	5	8	309
8	14	0	4	9	0
9	0	2	23	20	180
		4	39	39	0
		5	9	10	90
		6	38	33	180
		7	12	8	270
		8	8	6	0
		10	17	16	180
		11	18	14	270
9	1	0	15	10	90
9	2	0	25	29	270
9	3	0	17	20	270
9	4	0	13	13	270
9	5	0	16	15	270
9	7	0	17	17	90
9	9	0	15	14	90
9	11	0	8	7	270
10	0	0	33	33	0
		3	42	39	90
		4	24	23	0
		6	11	7	0
		7	33	32	90
		8	7	8	0
		10	10	12	0
		12	6	6	0
10	1	0	25	24	0
10	2	0	16	18	0
10	3	0	31	33	0
10	7	0	13	12	180
10	0	2	10	10	180
		4	20	18	0
		6	24	21	180
		8	20	20	0
10	11	0	23	30	90
11	1	0	23	27	270
11	3	0	10	13	270
11	5	0	20	27	270
12	0	0	9	6	180
		2	7	9	180
		3	19	20	90
		4	9	9	180
12	1	0	15	13	0
12	3	0	18	21	0

A C K N O W L E D G E M E N T S.

In conclusion the author would like to thank his supervisor Prof. J.M. Robertson, C.B.E., F.R.S., for his interest and encouragement and also Dr. S.C. Abrahams, his original mentor in the subject of X-ray crystallography and who has very kindly arranged to have several calculations carried out which would have been impossible with the computing equipment at the author's disposal.

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J.V. Silverton
Summary of Thesis

This thesis embodies the results of investigations into two dissimilar aspects of X-ray crystallography, hence the rather general title " Studies in Crystal Structure ".

The first part concerns a study of the crystal structure of Tris (methylsulphonyl) methane, a somewhat unusual organic compound, which is an acid of strength comparable with hydrochloric acid. Two aspects of this structure are of interest, firstly the molecular geometry, because of theoretical speculation previous to the work, and secondly the fact that the crystals give rise to an unusual form of diffuse scattering of X-rays.

That the two aspects are not independent was shown in the course of the investigation. It was impossible to account for the intensities of the Bragg reflexions on a basis of any ordered structure. These intensities can only refer to a structure which is an average taken over the whole crystal and the nature of this 'average structure' was deduced, after much work in two dimensions, by the use of three-dimensional data and vector and Fourier methods. The average structure involves partial occupancy of sites in the unit-cell whose positions are related by a centre of symmetry, not required by the space-group. The two sites do not appear to be occupied equally.

The results of a least-squares refinement of the average structure are given. The residual is 9% and thus the molecular structure is known to a fair degree of accuracy. The structure appears to contradict the previously mentioned theoretical ideas. The bond lengths and angles are comparable with those in similar compounds.

The nature of the average structure has been used as a starting point for investigations of the disorder with the help of an optical diffractometer. Details are given of the finding of a fairly small unit which gives rise to an optical transform similar to the X-ray photographs. The extension of this model to the whole crystal is also considered.

The second part of the thesis concerns work in a more conventional field of crystal chemistry; that of alkaloid structure.

Details are given of the investigation of the crystal structure of the alkaloid Calycanthine, derived from the poisonous shrub, Calycanthus aureus.

The structure of this compound was known only partially at the start of the work. The structure was studied initially by two-dimensional methods and, while partial success in the location of the atoms in the crystals of the hydrobromide of the alkaloid was attained by the method of 'generalized projections', the crystal structure was not solved completely until three-dimensional methods, using the 'heavy-atom' technique, were employed.